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# **Harakeke Fibre as Reinforcement in Epoxy Matrix Composites and Its Hybridisation with Hemp Fibre**

A thesis  
submitted in fulfilment  
of the requirements for the degree  
*of*  
***Doctor of Philosophy***  
***in Materials and Process Engineering***  
*at*  
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*by*  
***Le Minh Tan***



THE UNIVERSITY OF  
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## **Abstract**

Over the last few decades, due to increasing global awareness of environmental issues, there has been great interest and motivation in research to develop natural fibre composites to replace glass fibre composites in certain applications. Harakeke fibre known as New Zealand flax or *Phormium tenax* used to be an important export material in New Zealand in the early twentieth century, but its production reduced due to the availability of synthetic fibres midcentury and competition from other natural fibres such as sisal and flax. Now, harakeke plants are planted mainly for landscaping with some fibre extracted from harakeke leaves used for craft goods and traditional products of Maori people who were the earliest settlers in New Zealand. Only two family workshops in the country are currently extracting harakeke fibre for this purpose. The aim of this thesis was to assess if harakeke fibre has potential for reinforcement in polymer composites and to assess the hybridisation of harakeke/hemp hybrid composites.

Both short and long fibres were used as reinforcement, while a low viscosity epoxy resin was used as the matrix. Short fibres were alkali treated before being used to reinforce epoxy, while long fibres were used as supplied. Short and long fibres were aligned using dynamic sheet forming and manual carding, respectively. Composites were produced using hand lay-up and compression moulding. The physical and mechanical properties of fibres and composites were tested following ASTM and ISO standards. The surfaces of fibres and fracture surfaces of composites were assessed microscopically using optical microscopes and scanning electron microscope (SEM).

Short harakeke and hemp fibres were alkali treated at elevated temperatures in a fibre pulping digester with a solution of 2wt% NaOH or 5wt% NaOH/2wt% Na<sub>2</sub>SO<sub>3</sub>. Single fibre tensile testing was carried out on untreated and treated fibres. It was found that harakeke fibre treated with NaOH and hemp fibre treated with NaOH/Na<sub>2</sub>SO<sub>3</sub> retained their tensile strength and Young's modulus compared to the untreated, while harakeke fibre treated with NaOH/Na<sub>2</sub>SO<sub>3</sub> was degraded. Fibre surfaces and fibre separation were evaluated revealing that fibres treated with NaOH/Na<sub>2</sub>SO<sub>3</sub> had better separation and rougher surfaces compared to those treated with NaOH. Densities of harakeke and hemp were found to increase after alkali treatment. Fibre lumens were found to make up significant volume of fibres with 41% of single fibre volume and 21% of fibre bundle volume for harakeke fibre and 18% and 11% for hemp fibre, respectively. Lumens were found to be a major factor contributing to porosity of long aligned harakeke composites.

Mechanical properties including tensile, flexural and fracture toughness of composites containing aligned short 2%NaOH treated harakeke fibre with different fibre contents were evaluated and compared with randomly oriented harakeke/epoxy composites. It was found that all properties increased with fibre content. Tensile strength and Young's modulus of the aligned short fibre composites at the optimum fibre content of 46wt% were 136 MPa and 10.5 GPa, respectively. These values are higher than any reported in the literature to date for natural fibre composites excluding those where hand-layup or a continuous fibre form has been produced and furthermore, these values overlap with those achieved using these procedures.

Mechanical properties of aligned long harakeke composites were also evaluated. The tensile strength and Young's modulus were comparable to those for sisal and hemp composites in the literature and their specific values were comparable to those for glass fibre composites. Impact strength and fracture toughness of harakeke fibre composites that have not been seen previously in the literature were found to be  $132 \text{ KJ/m}^2$  and  $7.69 \text{ MPa.m}^{-1/2}$ , respectively, at a fibre content of 63wt% for aligned long harakeke/epoxy composites. These values are higher than any reported in the literature to date for natural fibre polymer composites. A Rule of Mixtures based model was developed for predicting aligned long harakeke fibre composite strength with the assumption that composites fail when fibres with the lowest failure strains failed and considering the effect of porosity. It was found that porosity affected tensile strength as well as Young's modulus of the composites.

Aligned long or short harakeke/hemp hybrid biocomposites were prepared with different fibre lay-up and weight ratios between harakeke and hemp and their mechanical properties were assessed. While tensile properties, impact strength and fracture toughness ( $K_{IC}$ ) of the harakeke/hemp hybrid biocomposites were found to be independent on fibre lay-up, flexural properties were found to be dependent as would be expected due to the influence of second moment of area. The fibre failure strain based hybrid effect (FS hybrid effect) defined as the enhancement of low elongation fibre due to presence of high elongation fibre in composite and the Rule of Mixtures based hybrid effect (ROM hybrid effect) termed as the deviation of a certain property from the Rule of Mixtures were assessed for harakeke/hemp hybrid biocomposites. While the FS hybrid effect was found not to be observed, ROM positive hybrid effects were found to be observed

for fracture toughness of aligned short harakeke/hemp hybrid biocomposites with different fibre lay-ups and different relative fibre contents. ROM positive hybrid effects were also found to be observed for flexural modulus for comingled harakeke/hemp fibre composites at different relative fibre contents. Tensile properties and impact strength were found to obey the Rule of Mixtures.

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## **Publications**

### **The potential of harakeke fibre as reinforcement in polymer matrix composites including modelling of long harakeke fibre composite strength**

TM Le, KL Pickering

Composites Part A: Applied Science and Manufacturing. Vol: 76 Pages: 44-53  
Published 2015

### **High performance aligned short natural fibre - epoxy composites.**

KL Pickering, TM Le

Composites Part B: Engineering. Vol 85 Pages 123-129 Published 2016.

### **A review of recent developments in natural fibre composites and their mechanical performance**

KL Pickering, MG Aruan Efendy, TM Le

Composites Part A: Applied Science and Manufacturing. Vol 83 Pages 98-112  
Published 2016.

### **The mechanical properties of epoxy based hybrid biocomposites reinforced with harakeke and hemp fibres**

TM Le, KL Pickering

Proceeding Composites Australia and CRC-ACS, 2013 Composites Conference & Trade Show Published: 2013

### **The manufacture and mechanical properties of aligned long harakeke fibre reinforced epoxy composites**

**TM Le**, KL Pickering

Proceeding 11th International Conference on Flow Processing in Composite Materials Published: 2012



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# Symbols and abbreviations

## Symbols

$\epsilon_c$	Composite failure strain (%)
$\epsilon_{c1}$	Composite strain at point 1 (%)
$\epsilon_{c2}$	Composite strain at point 2 (%)
$\epsilon_m$	Matrix strain (%)
$\rho$	Density (g/cm <sup>3</sup> )
$\rho_f$	Fibre density (g/cm <sup>3</sup> )
$\rho_{sf}$	Single fibre density (g/cm <sup>3</sup> )
$\rho_{fb}$	Fibre bundle density (g/cm <sup>3</sup> )
$\rho_m$	Matrix density (g/cm <sup>3</sup> )
$\sigma$	Fibre stress (MPa)
$\sigma_c$	Composite strength (MPa)
$\sigma_{c2}$	Composite stress corresponding to $\epsilon_{c1}$ (MPa)
$\sigma_{c1}$	Composite stress corresponding to $\epsilon_{c1}$ (MPa)
$\sigma_f$	Mean fibre tensile strength (MPa)
$\sigma_m$	Matrix stress or tensile strength (MPa)
$\tau$	Interfacial shear strength (MPa)
$\Delta l$	Actual fibre elongation (mm)
$\Delta L$	Cross-head displacement (mm)
$A$	Average fibre cross sectional area (m <sup>2</sup> )
$A_l$	Cross sectional area of lumen ( $\mu^2$ )
$A_{sf}$	Average cross sectional area of single fibres ( $\mu^2$ )
$C_s$	System compliance (mm/N)
$D$	Fibre diameter ( $\mu\text{m}$ )
$D_l$	Lumen diameter ( $\mu$ )
$D_f$	Fibre diameter ( $\mu$ )
$E_f$	Fibre Young's modulus (GPa)
$E_m$	Matrix Young's modulus (GPa)
$F$	Applied force (N)
$F_{\max}$	Peak force (N)

$k_1$	Fibre orientation factor
$k_2$	Fibre length factor
$l_0$	Gauge length in single fibre tensile testing (mm)
$L$	Average fibre length (mm)
$L_c$	Critical fibre length (mm)
$L_c/D$	Critical aspect ratio
$m_{sf}$	Mass of single fibres (g)
$m_{fb}$	Mass of fibre bundles (g)
$P_f$	Probability of failure
$r$	Fibre radius ( $\mu\text{m}$ )
$T_w$	Fibre cell wall thickness ( $\mu$ )
$v_l$	Average volume of lumen ( $\mu^3$ )
$v_{sf}$	Average volume of single fibres ( $\mu^3$ )
$v_{fb}$	Average volume of fibre bundles ( $\mu^3$ )
$V_f$	Fibre volume fraction
$V_i$	Volume fraction of the sub-critical fibre lengths
$V_j$	Volume fraction of the super-critical fibre lengths
$V_l$	Average lumen volume fraction in single fibres
$V_l'$	Average lumen volume fraction in fibre bundles
$V_m$	Matrix volume fraction
$W_f$	Fibre weight fraction
$Y_p$	Pulp yield

## Abbreviations

AE	Acoustic emission
ANOVA	Analysis of variance
ASTM	American Society for Testing and Materials
CFM	Confocal fluorescent microscopy
CD	Cross direction
CrI	The crystallinity index
FESEM	Field emission scanning electron microscope
FS	Fibre failure strain
FTIR	Fourier transform infrared spectroscopy
IS	Impact strength
GPa	Gigapascal
IFSS	Interfacial shear strength
LTS	Longitudinal tensile strength
MD	Machine direction
MPa	Megapascal
NaOH	Sodium hydroxide
Na <sub>2</sub> SO <sub>3</sub>	Sodium sulphite
NFC	Natural fibre composites
OH	Hydroxyl groups
PE	Polyethylene
PEEK	Polyetheretherketone
PLA	Poly lactic acid
PMC	Polymer matrix composite
PP	Polypropylene
PVC	Polyvinylchloride
SEM	Scanning electron microscope
THC	Tetrahydrocannabinol
TS	Tensile strength
TTS	Transverse tensile strength
UK	United Kingdom
UP	Unsaturated polyester

VE

Vinyl ester

YM

Young's modulus

# **Chapter One: Introduction**

## **1.1 Composite materials**

Material scientists have been striving to create materials with reduced weight and higher stiffness and strength at lower cost in order to improve performance for different applications. The most successful group of materials is that of composites. A composite can be considered as a mixture of two or more distinct constituents or phases and simultaneously satisfies three criteria: (i) the proportion of each constituent is greater than 5%; (ii) constituents have different properties and the composite properties are significantly different from those of constituents; (iii) constituents are intimately mixed and combined by various means [1].

Different constituents of a composite are separated by a distinct interface which can be observed on a microscopic scale. The continuous constituent that often presents the greater fraction in the composite is termed the matrix and it can be ceramic, metallic or polymeric. Whereas, the other constituent that improves the mechanical properties of the matrix is termed the reinforcement or reinforcing phase. The reinforcement is usually stronger, stiffer and harder than the matrix and it can be either fibrous or particulate. The reinforcement enhances the mechanical properties of the matrix while the matrix plays a role of adhering fibres together and transferring applied stresses from the composite to the fibres via the interface.

Using composites is not a really new or recent idea. Bricks made from straw reinforced mud, which were used in ancient civilization thousands years ago, can be considered as composites. In the 20<sup>th</sup> century, composites had developed and

proved their potential to replace metal in many applications. In the early 1960s, the development of carbon fibres in the UK and boron fibres in the USA led to the rapid expansion of synthetic composite production involving combination of fibres and various polymer[1]. Polymer matrix composites possess low density, a distinct benefit over metals, resulting in the improvement of Young's modulus per unit mass (specific modulus) and tensile strength per unit mass (specific strength). This allows reduction of the weight of components which is especially important for moving parts because it can result in energy saving and cost reduction. Low density is also an advantage of composites when utilized in structural engineering.

Synthetic fibres are not only used as reinforcement of single-fibre composites but combined with another synthetic fibre to make hybrid composites. A hybrid composite is a composite which have two or more different fibres incorporated in a common matrix. In principle, several different types of fibres can be incorporated into a hybrid system but in practice it is likely that a hybrid composition of only two types of fibres would be most useful [2]. By mingling two or more types of fibre in a resin to form a hybrid composite, it may be possible to produce a material holding the combined benefits of the individual components and simultaneously moderating their less desirable qualities. Furthermore, it is able to tailor the properties of such materials to suit specific requirement [2]. A combination of carbon and glass fibres [2-4] into the same polymeric matrix to create hybrids is the most common. Carbon fibre provides strong, stiff and low density reinforcement but is relatively expensive and brittle, whilst glass fibre is relatively cheap and has better fracture toughness property but its strength and stiffness are relatively disadvantageous. By incorporating two types of fibres into a polymer matrix, it may be possible to achieve a balance



between the properties of all-carbon fibre and all-glass fibre composites [4]. In 1972, Hayashi [3] reported that the failure strain of carbon fibre in carbon/glass reinforced epoxy hybrid composite was 40% higher than that in carbon/epoxy composite. This increase of the failure strain of carbon fibre was considered as the hybrid effect. Therefore, the most basic definition of the hybrid effect is the enhancement of the failure strain of the lower elongation reinforcement when part of a hybrid composite. Another definition of the hybrid effect is a deviation of a certain property from the rule of mixtures.

## **1.2 Natural fibre composites**

Carbon and aramid fibres are commonly used as reinforcement for composites that require high performance with extremely high strength and stiffness such as airplane parts or sport gears. However, they are too expensive to apply in many applications. In this case, glass fibres are ideal alternatives due to their benefits over carbon and aramid fibres including lower cost, acceptable strength and stiffness as well as relative ease of manufacture. Actually, glass fibres have been dominating the composite industry to date in terms of quantities used.

The use of natural fibres as reinforcement in polymer matrix composites to replace synthetic fibres, especially glass fibres, has been increasing because of growing environmental awareness and their advantages over synthetic fibres such as low cost, low density, high specific properties and abundant availability. Recent research findings have shown that, in certain composite applications, natural fibres have demonstrated competitive performance to glass fibre, a dominant fibre used in composites [5; 6]. Composites made from natural fibres

and polymer matrices (petroleum-derived polymers or biopolymers) are termed biocomposites.

Natural fibre can be derived from minerals, animals or plants. Asbestos fibres comprised of mineral based natural fibres have been widely exploited to reinforce plastics and cements but are now banned in many countries due to their hazard to health if ingested. Generally, plant based fibres are much stronger and stiffer than animal based fibres. Spider silk is an exception with very high strength but it is relatively expensive and less readily available. Moreover, plant fibre can be cultivated in many countries with different climate and be harvested after short periods. These make plant based fibres more widely used in composites. The selection of natural fibres for composites mainly depends on their mechanical properties, availability and price. Flax and hemp are the most common plant fibres used in composites due to their higher strength and stiffness than other plant fibres. Moreover, they are available in Europe, the centre of research and application of biocomposites. Research in Asia and South America has focused on fibres that are available in these places such as jute and sisal including for use in composites. These fibres have moderate strength and stiffness but are much cheaper than flax and hemp [7]. In the last decade, further natural fibres have been introduced to composite area such as pineapple leaf fibre, oil palm, coir, bagasse fibres. These fibres are waste materials from agriculture, so they are expected to be cheap raw material sources. However, their low strength and stiffness might be challenging for them to be applied in the composite industry. Harakeke fibre or *Phormium tenax* (commonly known as New Zealand flax) is also being considered to be used in structural applications in New Zealand due to its good mechanical properties and its local availability there.

The most common matrices for bicomposites are polymeric including thermosetting polymers (thermosets) and thermoplastic polymers. Thermoplastics readily flow under stress at elevated temperatures, so they can be fabricated into the required components, and then become solid and retain their shape when cooled to the room temperature. These may be repeatedly heated, fabricated and cooled, and consequently scrap may be recycled. Common thermoplastics include acrylic, nylon, polypropylene (PP), polystyrene, polyethylene (PE), polyvinylchloride (PVC) and polyetheretherketone (PEEK). Thermosets have cross-linked or network structures with covalent bonds between all molecules. They do not melt but decompose when heated and thus they cannot be thermally reshaped. Thermosets are generally brittle at room temperature and having low fracture toughness. On the other hand, their stiffness, softening temperatures and creep properties are higher than thermoplastics due to cross-linking. Their resistance to chemical attack is also better than thermoplastics. Common thermosetting resins include unsaturated polyester (UP), epoxy, phenol formaldehyde and vinyl ester (VE) resins. Plant fibres used as reinforcement in bicomposite start losing mass noticeably at about 200-220°C; above this temperature irreversible degradation of the fibres occurs [8], although under some circumstances it is possible for them to be processed at higher temperature for a short period of time [9]. Therefore, this limits the selection of matrices for biocomposites. Only thermoplastics with melting point below this temperature such as polyethylene PE, PP, PVC and polystyrene and thermosets (which can be cured below this temperature) are useable as a matrix [10].

Plant fibres have been also combined with another natural or fibre glass fibre to make hybrid biocomposites. The latter is more common as it allows greater

improvement in most mechanical properties due to superior mechanical properties of glass fibre over those of natural fibres. When two natural fibres are combined the focus is often to obtain a better balance in physical, mechanical and chemical properties rather than exploiting the hybrid effect [11]. Research in hybrid biocomposites often deals with random mats and short fibres that make hybrid effect more difficult to find. In this work, aligned long (short) harakeke fibre and aligned long (short) hemp fibre were combined to produce hybrid biocomposites and see if hybrid effect would be exploited.

### **1.3 Research objectives**

The aim of the project is to assess if harakeke fibre has potential as reinforcement for composite materials and if the hybrid effect would be exploited when combined with hemp fibre in hybrid biocomposites.

The specific objectives of the work are summarised as follows:

- to gain understanding of harakeke fibre reinforced polymer composites and natural fibre hybrid biocomposites,
- to improve fibre separation and dispersion in composites by means of alkali fibre treatments,
- to enhance orientation of short fibres in epoxy matrix composites by means of dynamic sheet forming,
- to evaluate the performance of aligned long harakeke fibre reinforced epoxy composites produced in this study and compare the experimentally obtained composite strengths and Young's modulus with theoretical composite strengths obtained by means of mathematical modeling including the effect of porosity in the composites on their tensile properties,

- to evaluate the performance of aligned short harakeke fibre reinforced epoxy composites and the effect of different fibre treatments on mechanical properties of the composites and assess fibre orientation,
- to evaluate mechanical properties and hybrid effect of aligned long (short) harakeke/hemp hybrid biocomposites.

## **Chapter two: Literature review**

### **2.1 Natural fibres**

#### **2.1.1 Introduction**

Natural fibre can be derived from mineral (inorganic), animal and plant (organic) sources. Asbestos are mineral based natural fibres which were widely exploited to reinforce plastics and cements but they are now banned in many countries due to their hazard to health if ingested, so they are not mentioned further here. All plant fibres contain cellulose as their major structural component, whereas animal fibres mainly consist of protein. According to the origin of the fibre, organic fibres can be classified into the following categories:

- Bast fibres: flax, hemp, jute, ramie and kenaf. These fibres are extracted from the bark of the stems of dicotyledonous plants
- Leaf fibres: sisal, pineapple, harakeke, henequen, banana and abaca. These fibres are extracted from monocotyledonous plants.
- Seed and fruit fibres: cotton, kapok, oil palm and coir. These fibres come from seed or fruit hairs.
- Grasses and reeds: these fibre are found in the stem of some plants such as bamboo, alfa and sugar cane (bagasse fibre)
- Animal fibres: These fibres can be either wool coming from the fleece of some farmed animal such as sheep, alpaca and goat or silk from the cocoon of silkworm (*bombyx mori*) or feather fibre from the feather of domestic birds such as chickens and ducks.

**Table 2.1: Price , production and application of natural fibres [12; 13]**

Fibre	Price of raw fibre (US\$/kg)	Million tonnes	Application	Main producer countries
Cotton	1.5-2.2	25	Textile fabric: apparel (60%), home furnishing, upholstery, non-wovens, specialty paper, cellulose, medical and hygienic supplies (hydrophilic absorbents)	China, USA, India, Pakistan, Australia
Jute	0.35	2.5	Hessian, sacking and carpet backing	India, Bangladesh
Flax	0.5-1.5	0.5	textile fabric, composites, non-woven, insulation mats and specialist paper	China, France, Belgium, Spain, Belarus, Ukraine
Kenaf	-	0.45	Hessian, sacking and carpet backing	China, India, Thailand
Coir	0.25-0.5	0.45	Twine, ropes, carpets, brushes, mattress, geotextiles and horticultural products	India, Sri Lanka
Sisal	0.6-0.7	0.30	Twine and ropes	Brazil, China, Indian, Tanzania, Kenya
Ramie	1.5-2.5	0.15	Textile fabric	China
Hemp	0.6-1.8	0.10	Textile fabric, composites, non-woven, insulation mats, specialist paper	China, Spain, France, Germany
Apaca	-	0.10	Speciality paper and tea bags	Philippines, Ecuador
Henequen	-	0.03	Twine and ropes	Mexico
Kapok	-	0.03	Pillow and mattress	Indonesia

As seen in Table 2.1, most plant fibres are cultivated in tropical climatic regions (i.e. South and Southeast asia, USA, Africa and Australia) and fewer fibres in

temperate climate areas (i.e. Europe and China) such as flax and hemp. Production and common applications of some natural fibres are also summarised in Table 2.1. It can be seen that cotton is produced the most which is not surprising given that cotton is the most popular natural fibre used in the textile industry, which has very high demand of fibres. The other fibres are mainly used in textiles, ropes and packaging.

The application of natural fibres in composites is not a really new or recent idea. However, the research and application of natural fibres as the reinforcement for composites has taken off in the last two decades due to growing environmental awareness alongside the advantages of natural fibres over synthetic fibres such as low cost, low density, high specific properties and abundant availability as indicated in Table 2.2

**Table 2.2: Comparison between natural and glass fibres [6]**

	Natural fibres	Glass fibres
Density	Low	Twice that of natural fibre
Cost	Low	Low, but higher than natural fibre
Renewability	Yes	No
Recyclability	Yes	No
Energy consumption	Low	High
Distribution	Wide	Wide
CO <sub>2</sub> neutral	Yes	No
Abrasion to machines	No	Yes
Health risk when inhaled	No	Yes
Disposal	Biodegradable	Not biodegradable



A huge number of studies [7; 14] have reported on the use of natural fibres in composites and have proved their potential to replace glass fibres in certain applications which do not require very high strength. Wambua et al [6] looked at mechanical properties of some plant fibres (kenaf, hemp, jute, sisal and coir) reinforced polypropylene composites and compared them to glass fibre mat reinforced polypropylene composites and found that mechanical properties of the natural fibre composites are comparable to those of the corresponding glass fibre mat composites. The specific properties in some cases were even better than those of the glass fibre composites. The authors suggested that natural fibre composites have the potential to replace glass in applications that do not require very high load bearing capabilities.

Generally, plant based fibres are much stronger and stiffer than animal based. Spider silk is an exception with very high strength, but it is relatively expensive and less readily available. Moreover, plant fibre can be cultivated in many countries with different climates and be harvested after short periods. These make plant based fibres more widely used in composites.

However, plant fibres have some issues which should be considered when used as the reinforcement for composites [7]:

- variability of properties, which can cause variability of composite properties and difficulty in prediction composite properties,
- fibre grown in bundles within plants which need to be degummed and separated in some cases for better fibre dispersion in composites,
- plant fibres contain amorphous materials which should be removed for better composite properties,

- incompatible between fibre and matrix that requires fibre and (or) matrix modification for better composite properties,
- plant fibres ease to absorb water, which can affect the dimensional stability and properties of composites,
- low thermal stability, which can limit processing temperature of composites.

Some of these issues would be discussed further in Sections 2.1.5.

**Table 2.3: Compositions of different plant fibres [15]**

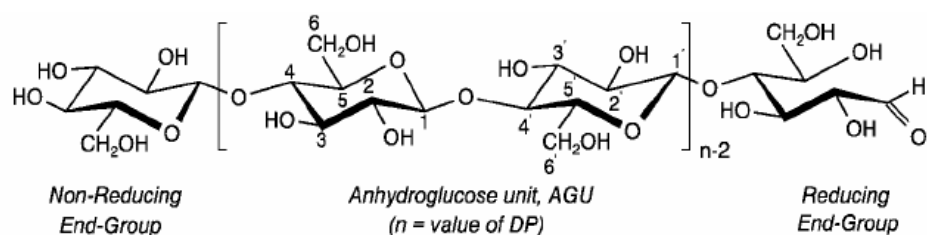
Type of fibre	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)	Pectin (wt%)	Moisture content (wt%)	Wax (wt%)	Microfibrillar angle(°)
<b>Bast fibre</b>							
Flax	64.1-71.9	16.7-20.6	2.0-2.2	1.8-2.3	8-12	1.7	5-10
Hemp	70.2-74.4	17.0-22.4	3.7-5.7	0.9	6.2-12	0.8	2-6.2
Jute	61-71.5	12.0-20.4	11.8-13	0.2	12.5-13.7	0.5	8
Kenaf	31-57	21.5	8-19	3-5			
Ramie	68.6-76.2	13.1-16.7	0.6-0.7	1.9	7.5-17	0.3	7.5
<b>Leaf fibre</b>							
Sisal	65.8-78	8-14	10-14	0.8-10	10-22	0.2	10-22
Harakeke	45.1-72.0	30.1	11.2	0.7	10.0	0.7	
Henequen	77.6	4-8	13.1				
Pineapple	70-82		5-12.7		11.8		14
Banana	63-64	10-19	5		10-12		11
<b>Seed or fruit fibre</b>							
Cotton	82.7-90	5.7		0-1	7.85-8.5	0.6	
Coir	32-43	0.15-0.25	40-45	3-4	8		30-49

### 2.1.2 Natural fibre constituents

The basic constituents of plant-based fibres are cellulose, hemicelluloses, lignin and pectin (in some cases) and a small amount of wax. The amount of components present is shown in Table 2.3.

#### Cellulose

Cellulose, which is the dominant constituent of all plant fibres, was discovered and named by French chemist Anselm Payen in 1838 [16]. It is generally accepted that cellulose is a linear polymer consisting of D-anhydroglucose monomer units ( $C_6H_{12}O_6$ ) (so-called D-glucopyranose units) which are joined together by  $\beta$ -1,4-glycosidic linkages [17] as shown in Figure 2.1.

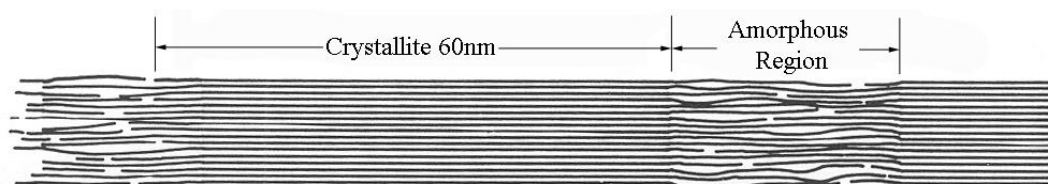


**Figure 2.1: Molecular structure of cellulose [18]**

The anhydroglucose units do not lie exactly in plane, but assume a chair conformation, with successive glucose residues rotated through an angle of  $180^\circ$  about the molecular axis. The polymer chain contains free hydroxyl groups (OH) at the C-2, C-3, and C-6 atoms (Figure 2.1). These OH groups form hydrogen bonds between chains and within chains which determine the rigidity and strength of cellulose and cellulose based material [19]. The OH groups of celluloses can easily hydrogen bond with hydroxyl groups. This explains why all of plant fibres have hydrophilic nature.

Although different natural fibres have the same molecular structure of cellulose, the degree of polymerization (DP) varies. The DP expresses the length of the polymer which varies depending on the type of natural fibre.

Cellulose is made of crystalline and amorphous regions [20] as shown in Figure 2.2, which can occur naturally called type I or can be regenerated, but results type II [17]. In crystalline regions, there are limited inter-chain OH groups available for bonding with water molecules due to its closely packed structure. This makes crystalline cellulose less hydrophilic.

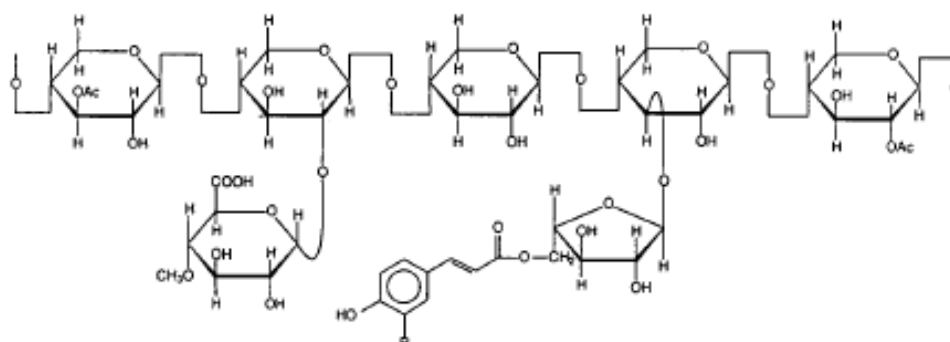


**Figure 2.2: Schematic representation of the crystallite structure of cellulose [20]**

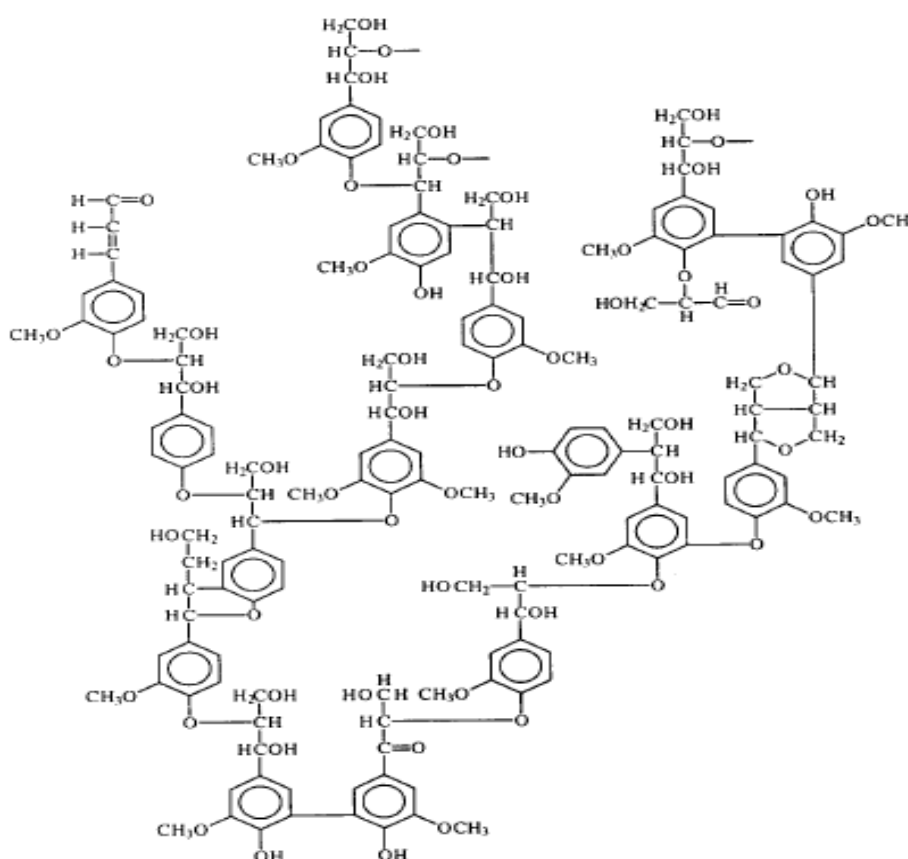
### **Hemicellulose**

Another main component of plant fibres is hemicellulose. The term “hemicellulose” is probably a misnomer since it is not a form of cellulose at all but belongs to a group of polysaccharides that remains attached to cellulose after lignin has been removed. Hemicellulose differs from cellulose in three important aspects. Firstly, hemicellulose contains several different sugar units as shown in Figure 2.3 whereas cellulose contains only D-anhydroglucose units. Secondly, hemicellulose is a highly branched polymer compared to the linearity of cellulose. Finally, the DP of cellulose is ten to one hundred times higher than that of hemicellulose. Hemicellulose functions as a linkage between cellulose and lignin.

Due to its amorphous structure, its hydroxyl groups are much more accessible to water than those of cellulose [21]



**Figure 2.3: The structure of hemicelluloses [21]**



**Figure 2.4: Typical structure of lignin [21]**

## **Lignin**

Lignin is a complex hydrocarbon polymer with both aliphatic and aromatic constituents. The exact chemical nature of lignin is still not fully understood. There have not yet been any methods established to allow isolation of the lignin in its native state from the fibre. Lignin is considered to consist of three dimensional phenyl propane networks held together by ether and carbon-carbon bonds (Figure 2.4). Lignin has high molecular weight and complex structure, and thus it is insoluble in most solvents. Plant fibres usually have dark colour due to the double bonds in lignin. If lignin is oxidized and the double bonds are broken, the fibre will become lighter [21]. Lignin is a much less hydrophilic material than hemicellulose and cellulose. The mechanical properties of lignin are also lower than those of cellulose.

## **Pectin**

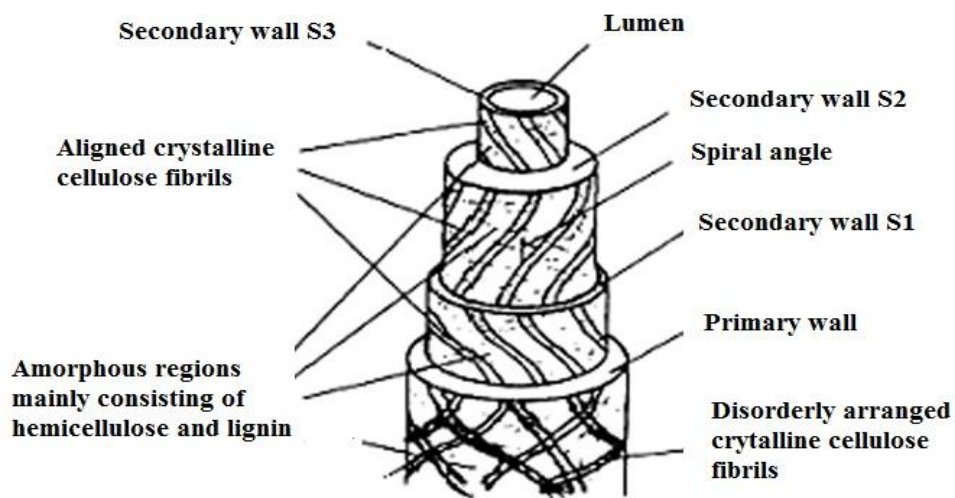
Pectins are located in the middle lamella and primary walls of plant fibres (See Figure 2.5). Pectin materials play an important role in binding the cell wall layers together in the fibre bundles. Removal of pectin material allows the separation of the fibre bundles from the surrounding cells of the stem [21].

## **Wax**

Wax in plant fibres consists of mainly long chain alkane, ester and alcohol. Esters and fatty acids are common but minor components, while the major portion of the wax is alcohols. The effect of the wax layer is to prevent water loss from a plant [21].

### 2.1.3 Physical structure of natural cellulose fibres

Plant fibres can be considered as composites of cellulose fibrils embedded in a matrix of lignin and hemicelluloses [22]. Each cell wall has a complex layered structure consisting of one thin primary wall, three secondary walls and a lumen at the centre as shown in Figure 2.5



**Figure 2.5: Physical structure of a cell wall of plant fibre [23]**

The thick middle secondary wall determines the mechanical properties of plant fibres [23]. Crystalline cellulose microfibrils are aligned parallel to each other within a layer and spiral around the cell axis. The angle between the fibre axis and the microfibrils is called the microfibrillar angle or spiral angles. Different fibres have different spiral angles. Such microfibrils have typically a diameter of about 10 - 30 nm and are made up of 30 - 100 cellulose molecules and provide mechanical strength to the fibre [23]. Microfibrils are held together by an amorphous matrix of lignin, hemicelluloses and pectin (in some cases). Hemicellulose acts as a cementing matrix due to its hydrogen bonds with cellulose

whilst Lignin plays a role as a coupling agent and increases the stiffness of the cellulose/hemicellulose composite [23]. Cell walls are bound together by a pectin rich intercellular material called middle lamella.

#### **2.1.4 Physical and mechanical properties of natural fibres**

Physical and mechanical properties of some natural fibres are presented in Table 2.4. Properties of plant fibres mainly depend on the structure, microfibrillar angle, cell dimensions and the chemical composition of fibres. Tensile strength and Young's modulus of fibres generally increase with increasing cellulose content and decreasing microfibrillar angle [24]. The properties of natural fibres vary considerably depending on chemical composition and structure [25], which relate to fibre type as well as fibre location, growing conditions, developmental stage or age, extraction method, treatment and storage procedures. Strength has been seen to reduce by 15% over 5 days after optimum harvest time [26] and manually extracted flax fibres have been found to have strength 20% higher than those extracted mechanically [19]. Flax fibre location in the stems has been found to influence the mechanical properties; the bottom fibres possess lower mechanical properties than the others while the middle fibres exhibit the best ones [25; 27]. A number of variables, which may have an influence on fibre mechanical properties are not always reported, including testing speed, gauge length and moisture content and temperature. Generally, strength increases with increasing moisture content and decreases as temperature increases [28]; the Young's modulus decreases with moisture content [27].



**Table 2.4: Mechanical properties of natural fibres compared with glass fibres [16; 29-31]**

<b>Fibre</b>	<b>Density (g/cm<sup>3</sup>)</b>	<b>Diameter (μm)</b>	<b>Failure strain (%)</b>	<b>Tensile Strength (MPa)</b>	<b>Young's Modulus (GPa)</b>	<b>Specific Tensile Strength (MPa/ gcm<sup>-3</sup>)</b>	<b>Specific Young's Modulus (GPa/ gcm<sup>-3</sup>)</b>
Flax	1.40-1.50	40-620	1.2-3.2	345-1830	27-80	230-1220	18-53
Hemp	1.40-1.50	16-50	1.3-4.7	550-1110	3-90	370-740	2-60
Jute	1.30-1.50	30-140	1.4-3.1	187-800	3-55	300-610	2-37
Ramie	1.50	40-60	3.6-3.8	400-938	44-128	270-620	29-85
Sisal	1.30-1.50	100-300	2.0-2.9	507-855	9.4-28	362-610	6.7-20
Abaca	1.5	17-21	10-12	980	72	653	48
Harakeke	1.3	13	-	805	21	618	16
Curaua	1.38	49-100	3.9	665-1404	20-36	482-1017	15-28
Pineapple	1.52-1.56	200-880	0.8-3.0	170-1627	6.21-82	112-1070	4-53
Banana	1.30-1.35	50-280	3-10	529-914	7.7-32	407-687	6-24
Henequen	1.49	20-500	3.0-5.0	430-580	10.1-16.3	289-389	7-11
Cotton	1.50-1.60	16-21	2.0-10	287-800	5.5-13	190-530	3.7-8.4
Coir	1.25-1.50	100-450	15-47	106-270	3-6	110-180	2-4
Alfa	1.40	19-35	1.5-2.4	188-308	18-25	134-220	13-18
Bagasse	0.55-1.25	200-400	0.9	20-290	2.7-17.0	36-232	5-14
Silk	1.30	-	15-60	100-1500	5-25	100-1500	4-20
Feather	0.90	-	6.9	100-203	3-10	112-226	3.3-11
Wool	1.30	-	13.2-35	50-315	2.3-5	38-242	1.8-3.8
E-glass	2.5-2.55	10-20	2.5	2000-3000	70	800-1400	29

As seen in Table 2.4, diameters specified for different fibres, which vary from some tens to some hundreds microns even in a type of fibre, can be for single fibres or bundles hence much variability can be seen in the literature. This should be also considered when comparing fibre properties from different sources. Calculation of properties is generally based on the total cross-section of a fibre or fibre bundle; however, single fibres have a central hollow lumen which takes up a significant proportion of the cross-sectional area, for example, 27.2, 6.8 and

34.0% for sisal, flax and jute respectively [28]. Therefore, fibre strength and Young's modulus would be underestimated when lumen is not taken account in the calculation.

## **2.1.5 Issues regarding the use of natural fibres in composites**

### ***2.1.5.1 Fibre separation and dispersion***

Ideal fibre dispersion implies that the fibres are fully separated from each other and each fibre is fully surrounded by the matrix. Poor fibre dispersion presents itself as agglomeration, resulting in an inhomogeneous mixture of resin-rich and fibre rich areas. The resin rich areas are weak, while the fibre rich areas (clumps) are susceptible to micro cracking. Micro cracks contribute to inferior mechanical properties of the composite. It is therefore necessary to ensure a homogeneous fibre distribution in order to achieve maximum strength and performance of the composite material.

Unlike glass fibres which are completely individualised in the composites and therefore have a relatively homogeneous distribution [32], plant fibres can have very low degree of individualisation due to their bundle structure with individual fibres being linked by pectin and lignin. To obtain good distribution and dispersion of fibres within a composite matrix, fibres need to be separated from each other which can be conducted using mechanical methods such as hackling [32] or alkali treatment at elevated temperatures [33]. Shearing forces generated in composite compounding equipments such as extruder and injection moulder can also separate fibres to some extent [34]. However, fibres can be damaged when processed on such equipment, resulting in reduction of fibre lengths depending on

temperature and time of processing, screw configuration and viscosity of melt mixture [35].

#### ***2.1.5.2 Moisture absorption***

Water in natural fibres can evaporate when processed at high temperature (about 100°C), resulting in the formation of porosity in composites. These pores can act as stress concentration points and can lead to premature failure of the composite during loading and thus reduce mechanical properties of composites. An increase of 10% of tensile strength and 20% of Young's modulus for jute/epoxy composites when the fibre was dried to a moisture content of 1% from 10% [36] prior to the composite processing has been reported. Natural fibre can absorb moisture during the service life of composites due to their hydrophilic nature. This causes fibre swelling and dimensional changes in the composites, particularly in the direction of fibre thickness [37]. The fibre swelling leads to reduction in the adhesion between the fibre and the matrix, and thus reduce the mechanical properties of the composites [38]. It has been found that exposure to moisture results in significant drops in tensile and flexural properties of hemp reinforced unsaturated polyester composites due to the degradation of the fibre–matrix interface [39]. Interfacial shear strength between bamboo fibre and vinyl ester matrix was found to decrease from 11 to 6.6 MPa when moisture content increased from 0 to 10% [40].

#### ***2.1.5.3 Thermal stability***

Plant fibres are inherently thermally unstable and start losing mass noticeably at about 200-220°C; above this temperature irreversible degradation of the fibres occurs [8], although under some circumstances it is possible for them to be

processed at higher temperature for a short period of time [9]. Therefore, this limits the selection of matrices for biocomposites. Only thermoplastics with melting point below this temperature such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC) and polystyrene and thermosets (which can be cured below this temperature) are useable as a matrix [10].

It has been found that the thermal stability of plant fibres can be improved by means of alkali fibre treatment [41-43] .

## **2.2 Matrix**

The matrix plays an important role in fibre reinforced composites transferring load to the reinforcement. Matrices can be either polymeric, metallic, carbon or ceramic. Polymeric matrices including thermersets and thermoplastics are used commonly for natural fibre composites. Thermoplastics readily flow under stress at elevated temperatures, so they can be fabricated into the required components, and then become solid and retain their shape when cooled to the room temperature. These may be repeatedly heated, fabricated and cooled, and consequently scrap may be recycled. Common thermoplastics include acrylic, nylon, polypropylene (PP), polystyrene, polyethylene (PE), polyvinylchloride (PVC) and polyetheretherketone (PEEK). Thermosets have cross-linked or network structures with covalent bonds between all molecules. They do not melt but decompose when heated and thus they cannot be thermally reshaped. Common thermosetting resins include unsaturated polyester (UP), epoxy, phenol formaldehyde and vinyl ester (VE) resins.

**Table 2.5: Summary of advantages and disadvantages of thermosetting and thermoplastic polymers [44]**

Property	Thermoset	Thermoplastic
Recyclability	Limited	Good
Young's modulus	High	Medium
Service temperature	High	Medium
Toughness	Medium	High
Viscosity	Low	High
Processing pressure	Low	High
Processing temperature	Low	High
Cycle time	Long	Short
Health concern	More	Less
Shelf life	Short	Long

Each polymer has its own advantages and disadvantages as shown in Table 2.5. Generally, thermosets are brittle at room temperature and have low fracture toughness. On the other hand, their stiffness, softening temperatures and creep properties are higher than thermoplastics due to cross-linking. Low viscosity is an important advantage of thermosets; it allows fibre thermosetting polymer composite to be processed at low even ambient temperatures with very good wetting between the fibre and matrix being obtain. Whereas, to lower the viscosity and gain better wetting, thermoplastic needs to be processed at high temperatures and pressure, resulting in more consumption of energy required. Moreover, as previously mentioned the upper limit processing temperature of plant fibre is about 200°C; only thermoplastic with melting point lower than this temperature (e.g. PE, PP and PVC) should be selected to manufacture plant fibre composites.

### 2.2.1 Epoxy

Epoxyes possess many desirable properties such as high tensile strength and modulus, excellent chemical and solvent resistance, dimensional and thermal stability, good creep resistance, and excellent fatigue properties and much of the early work used epoxy resins as matrix material for hybrid composites [45]. Epoxy resins are known to be able to form covalent cross-links with plant cell walls via -OH groups [46]; good adhesion between fibres and resin enables good reinforcement. In addition, epoxy resin does not produce volatile products during curing which is important in production of void free composites. Therefore, although epoxy resins are relatively more expensive than unsaturated polyesters, they have potential for the development of high added value biocomposites. Low viscosity epoxyes are preferable to choose to produce natural fibre composites due to their good impregnating characteristic.

The most popular epoxy monomer is that derived from the reaction of bis (4 - hydroxy phenylene) - 2,2 propane (called bisphenol A) and 1 - chloroprene 2 - oxide (called epichlorohydrin), in the presence of sodium hydroxide. The structure of the major product, bisphenol A diglycidyl ether (DGEBA or BADGE) is shown in Figure 2.6. Epoxy groups can react with amines, phenols, mercaptans, isocyanates or acids. Amines are the most commonly used curing agents or hardeners for epoxides [47].

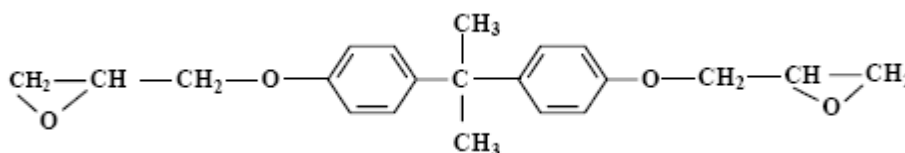
During curing, epoxy resins can undergo three basic reactions [48]:

1. Epoxy groups are rearranged and form direct linkages between themselves.
2. Aromatic and aliphatic -OHs link up to the epoxy groups.

3. Cross-linking takes place with the curing agent through various radical groups.

Unlike unsaturated polyester, epoxy resins undergo low polymerisation shrinkages during curing. The epoxy molecule also contains two ring groups at its centre, which are able to absorb both mechanical and thermal stresses better than linear groups, giving epoxy resin very good stiffness, toughness and heat resistance.

The primary disadvantages of the epoxy resins are that they require long curing times and, in general, their mould release characteristics are poor. Epoxy resins are characterised by their high adhesive strengths. This property is attributed to the polarity of aliphatic -OH groups and Ether groups that exist in both the initial resin and cured system. The polarity associated with these groups promotes electrostatic bonding forces between epoxy molecules and the polar fibres.



**Figure 2.6: Chemical structure of DGEBA**

As mentioned above, epoxy resin has many advantages when used as matrix of natural fibre composites as such it was chosen in the present project. Moreover, epoxy has been the most commonly used resin for hybrid composites and harakeke fibre composites, and therefore, the use of epoxy resin in this work allows comparing the research results with those reported in the literature.

## **2.3 Processing of thermosetting polymer composites**

There is a range of processing methods available for polymer matrix composites. These can be manual methods or automated methods. The method chosen depends on factors such as polymer, cost, and shape of component, number of components, performance required and availability. While injection moulding and hot pressing are the most widely used methods to process thermoplastic polymer composites, hand lay-up, compression moulding, filament winding, pultrusion and resin transfer moulding are commonly used for thermoset composites.

### **2.3.1 Hand lay-up**

In this method, the mould surface is treated with a release agent before placing fibre mat in the mould to avoid adhesion between the fibre mat and the mould surface. For epoxy resins, the liquid resin is mixed with a curing agent and poured onto the mat. A brush or roller is applied to work onto the mat. Curing is usually conducted at room temperature. Hand lay-up does not require complicated equipment. It is used particularly for small numbers of products and can be used for large components. However, low fibre content and difficulty in removing the trapped air are disadvantages of this method.

### **2.3.2 Compression Moulding**

Compression moulding of composites basically involves the pressing of randomly oriented or aligned fibre mats, either chopped or in continuous form with matrix material at ambient or elevated temperatures. In the case of processing thermosets, a fibre mat impregnated with thermoset resin is placed onto the bottom half of a compression mould cavity which can be pre-heated to the desired cure temperature. Then the top half of the mould is lowered at a constant rate until



the desired process pressure is reached and the saturated reinforcement is left curing in the mould. Once the composite has been cured, it is cooled and removed from the mould. Compressing moulding is used to produce large and relatively flat composite parts with good mechanical properties.

### **2.3.3 Filament winding**

In this method, a continuous strand of fibres is impregnated in a resin and then wound onto a rotating mandrel. After the resin has cured, the mandrel is withdrawn. Filament winding is suitable to manufacture cylindrical products such as chemical and fuel storage tanks, pipes, stacks, pressure vessels, and rocket motor cases.

### **2.3.4 Pultrusion**

In this process, a continuous strand of roving, mat, cloth or possibly with surfacing veil is impregnated in a resin bath, and then pulled through a steel die where the impregnated reinforcement is cured, the shape of composite is set and the fibre/resin ratio is controlled. This is a continuous process for the manufacture of products having a constant cross section, such as rod stock, structural shapes, beams, channels, pipe, tubing, fishing rods, and golf club shafts.

### **2.3.5 Resin transfer moulding**

In this process, the reinforcement is positioned in a closed and clamped mould and then resin is injected into the mould under pressure, using mix/meter injection equipment followed by the curing of the resin impregnated reinforcement in the mould. Vacuum assistance can be used to enhance resin flow in the mould cavity. This process can be automated and is capable of providing rapid cycle times.

In this project, the combination of hand lay-up and compression moulding was used to produce natural fibre reinforce epoxy composites. The equipments for these methods were available and suitable to process discontinuous reinforcement used in the project.

## **2.4 Hemp fibre and its composites**

Industrial hemp (*Cannabis sativa* L), which has been widely used in many civilizations, is an annual plant native to central Asia and known to have been grown in China over 4500 years ago. It probably reached central Europe in the Iron Age and there is evidence that it was grown in the UK by the Anglo-Saxons (800-1000 AD) [9]. Hemp is now grown mostly in China and some European countries as shown in Table 2.1. The flowering tops and to a lesser extent, leaves of hemp produce resin secretions containing the narcotic tetrahydrocannabinol (THC) which is available in marijuana [49]. This is the reason why industrial hemp was banned in many countries with the introduction of stricter drug laws [50]. In actual fact, the THC concentration produced by industrial hemp is only about 0.2% of the plant, so it cannot be used as a narcotic. In New Zealand, hemp cultivation was banned in the late 1930's, and this law was only amended in 2001 when nine growers were issued licenses to trial a crop of hemp for industrial use [51].

Hemp fibre is extracted from the bark on the stem of hemp plants. Like other plant fibres, the main constituents of the fibre are cellulose, hemicellulose, lignin and pectin as shown in Table 2.6. As can be seen, the chemical composition of hemp fibre published by different authors varies significantly, and such variability contributes to the variability of fibre properties as previously discussed.

**Table 2.6: Chemical composition of hemp fibres reported by various authors [49]**

Cellulose (%)	Hemicelluloses (%)	Pectin (%)	Lignin (%)	Other (%)
67.0	16.1	0.8	3.3	2.8
74.4	17.9	0.9	3.7	0.8
74.0	18.0	1.0	4.0	
55.0	16	18	4.0	7.0
76.0	11.5	1.3	3.2	
55-77			9-13	
75.1	<2		8.0	
70-74	17.9-22.4	0.9	3.7-5.7	0.8
75.6	10.7		6.6	
78.3			2.9	
76.1	12.3	1.6	5.7	3.3

Hemp is one of the strongest and stiffest fibres as shown in Table 2.4 and thus suitable for use in textiles, ropes and composites.

In 1941, hemp fibres along with flax fibres were used in resin matrix composites to produce the bodywork of a Henry Ford car, but the car did not make into general production due to economic limitations at that time [49]. The development of glass fibre and synthetic resins such as epoxies and unsaturated polyesters during and just after World War II led to the mass production of synthetic composites and the corresponding reduction in use of natural fibre composites. The interest in use of hemp fibre, like other natural fibres, in composites has been renewed in the last two decades due to the concern of environmental issues.

Application of hemp fibre as the reinforcement for composites has been mentioned in several review papers [7; 49; 52; 53]. Hemp fibre has been used to

reinforce thermoplastics, mainly polypropylene, and thermosets, mainly epoxy and unsaturated polyester.

## **2.5 Harakeke fibre and its composites**

Harakeke is the New Zealand native plant commonly known as New Zealand flax (botanical name: *Phormium tenax*) as shown in Figure 2.7. The name “flax” is actually a misnomer in describing *Phormium tenax* because it is not biologically related to European flax [54]. Moreover, harakeke fibres (shown in Figure 2.8) are extracted from the leaf whereas European flax fibres are obtained from the stem. Harakeke fibre has a long history of use for production of clothes, sacking and rope. Products of harakeke used to account for around 20% of the total export income of New Zealand in the early 1920s [54]. Sales decreased during the 20<sup>th</sup> century due to the presence of synthetic fibres and expansion of the sisal industry, and current use is confined to crafts [55].

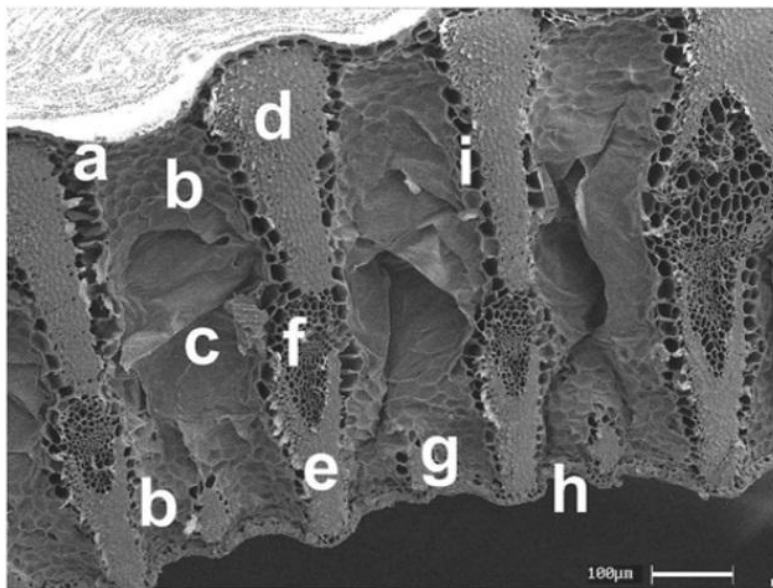


**Figure 2.7: A bush of harakeke plants**



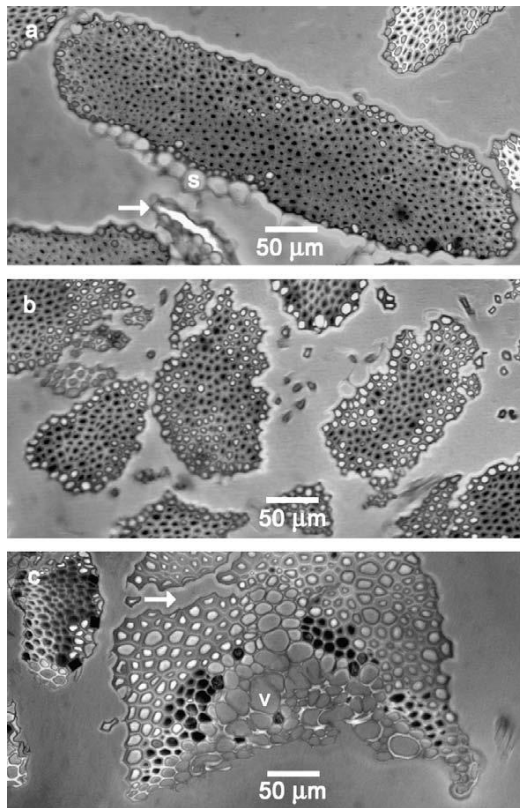
**Figure 2.8: Harakeke fibres**

Bundles of sclerenchyma structural fibres lie parallel to the middle ridge of the harakeke leaf but overlap each other in a spiral manner. Fibres are distributed evenly across the leaf as shown in Figure 2.9.



**Figure 2.9: Cross section of a harakeke leaf [56]: (a) upper epidermis, (b) parenchyma, (c) spongy parenchyma, (d) upper fibre bundle, (e) lower fibre bundle, (f) vascular bundle, (g) lesser fibre bundle, (h) lower epidermis, (i) fibre-bundle sheath cells**

As can be seen, fibre bundles are located at the upper and lower parts of the leaf in a pair with thin walled cells called vascular bundles at the centre. The cross section of the upper and lower bundles have been described as key-hole like shape and horseshoe shape, respectively [15]. There are also oval bundles of fibres located between the pairs of fibre bundles at the lower part of the leaf only called lesser fibre bundles. All of these fibre bundles are surrounded by very thin walled cells called sheath cells. Vascular bundles, sheath cells and sometime cuticle cells (epidermis) remain attached to fibre bundles and fibre bundles can be fragmented into different cross sectional shapes during processing as shown in Figure 2.10.



**Figure 2.10: Cross sections of harakeke fibre bundles imbedded in an epoxy resin [57]: (a) fibre bundle adhering sheath cells (labelled “s”) and cuticle material (arrow), (b) fragmented fibre bundles and separated fibre cells, (c) vascular bundles (labelled “v”).**

The chemical composition of harakeke fibre is summarised in Table 2.7. It can be seen that the hemicellulose content of harakeke fibre is higher than hemp and other plant fibres (see data in Table 2.3), resulting in a corresponding lower content of cellulose. Despite the low cellulose content, harakeke fibre has good mechanical properties. The tensile strength and Young's modulus of harakeke bundles were found to be 466-771 MPa and 24-28 GPa, respectively [58] and the average figures for individual fibres were 805 MPa and 21 GPa, respectively [59].

**Table 2.7: Chemical composition of harakeke fibre reported by different authors**

Cellulose	Hemicelluloses	Pectin	Lignin	Other	Ref
(%)	(%)	(%)	(%)	(%)	
60.9	27.3		7.8	24.0	[60]
45.1	30.1	0.7	11.2	0.7	[61]
53-55					[62]

Harakeke fibre has similar properties to sisal – another leaf fibre [54; 55]. While the application of sisal fibre in composites has been described by a variety of papers [63], harakeke fibre has just been studied recently for composites [15; 33; 54; 55; 57; 64; 65]. Hence, more studies are required on the use of harakeke fibre in polymer composites to see if it has potential to reinforce polymers. In the last decade, harakeke fibre has been considered to be used in composites in New Zealand due to its good mechanical properties and its local availability there.

One of the first studies on the use of harakeke fibre in composites was reported in 2007 [33]. In this work, pulped harakeke leaf fibre was used as the reinforcement for epoxy composites. The authors had found from the literature that improvement

in mechanical properties of composites reinforced with other leaf fibres relative to neat resin was not considerable [66-71]. This poor performance was considered due to leaf fibres being bundles of many fibre cells with 100 or more cells in a cross-section, with only a small number contributing to the fibre - matrix interface. Therefore, pulped harakeke fibre was selected in subsequent work with the expectation that all of the cells contributed to the fibre-matrix interface, which might lead to enhancement in mechanical properties of composites. Composites were prepared from both of pulped harakeke fibre and E-glass chopped strand for comparison. The results showed that pulped harakeke fibre can improve the flexural properties of an epoxy matrix. While the flexural modulus of the neat epoxy was just under 3 GPa, that of composites varied from around 6 GPa to about 8 GPa, increasing with fibre weight fraction as a linear function. The flexural strength of composites, from 120 MPa to 180 MPa, was also improved relative to about 90 MPa of the neat epoxy. The flexural modulus was comparable to that of the glass reinforced composite whilst the flexural strength was approximately two-thirds of that for the glass composite at a similar weight fraction. However, the flexural strength of pulped harakeke composites was still distinctly higher than that of composites reinforced with other leaf fibre reported before. In summary, pulped harakeke fibre had proved its potential for reinforcing thermosetting resin.

Newman et al [55] looked at epoxy resin composites reinforced with deacetylated harakeke fibre. Long harakeke fibres were treated with 1 % NaOH solution at 30°C to remove acetyl groups. Unidirectional composites were made from untreated and treated fibres (of the length 45 cm). Properties of the composite including water uptake and flexural were assessed. In terms of water uptake,



composites containing deacetylated fibre absorbed water more slowly than those containing untreated fibre. However, the composites reached the same equilibrium moisture content, regardless of whether the fibres were untreated or treated. The equilibrium moisture content increased with fibre content regardless of the treatment. The flexural modulus and flexural strength both increased with fibre content, and the differences between untreated and treated fibre were not distinct. The observed flexural properties were similar to those reported for unidirectional sisal fibre reinforced epoxy composites [72; 73]. Finally, the authors concluded that although high levels of acetylation do not influence the bending stiffness or strength they are not a useful feature of leaf fibres and need to be eliminated to reduce water uptake of the composites.

Research assessing failure mechanisms in unidirectional harakeke/epoxy composites was carried out by Newman et al [57]. Confocal fluorescent microscopy (CFM) and SEM were used to observe the morphology of harakeke fibre bundles, which were called technical fibres in the article, in the composites. The harakeke bundles were coarse fibres containing thick-walled fibre cells, surrounding sheath cells, cuticle, and vascular tissue. While thick-walled fibre cells were almost impermeable to epoxy resin, thin-walled cells such as sheath cells and vascular cells were almost entirely resin-filled. Fragmented technical fibres were also observed. The diversity of harakeke technical fibres was found to contribute to the complex failure mechanism of the harakeke/epoxy composites. The matrix was found to fail before the fibres due to the lower failure strain of epoxy (1.5%-1.7%) relative to harakeke technical fibres (2.4%-2.8%). Then, cracks propagated through low strength fibres such as resin-filled thin-walled cells then stopped when they encountered coarse bundles of thick-walled cells. Finally,

the authors recommended that it may be possible to improve tensile strength by choosing a cultivar possessing a low content of thin-walled bundle sheath cells or vascular cells, or changing the fibre extraction process to ensure a more uniform collection of technical fibres.

The effect of different methods of treatment including thermal, combinative alkaline-thermal, and combinative thermal-enzymatic-thermal treatments on harakeke fibre has been reported [54]. The fibres were instrumentally analysed using a wide angle X-ray spectroscopy (WAXS), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). All the treatments helped split the fibre bundles, enhance fibre surfaces, and remove some of the hemicelluloses and lignin. Of all the treatments, thermal-alkaline treatment produced the most promising results in term of cellulose content. The crystallinity index (CrI) of the harakeke fibres increased from 58.8% to 75.2% after thermal-alkaline treatment, and 64.7% and 67.8% for standard thermal treatment and thermal-enzymetic - thermal treatment, respectively. The fibre surfaces became rougher after all of the treatments. The fibre surface roughness was highest for the thermal-alkaline treatment compared to the others.

The use of harakeke in composites has attracted the interest of researchers outside New Zealand [15]. Mechanical and thermal properties of epoxy composites reinforced with untreated harakeke fibres have been investigated by researchers based in Italy. Composites containing 20 wt% randomly oriented short harakeke fibres and quasi-unidirectional long harakeke fibres were prepared using hand lay-up method and their mechanical properties were compared to neat epoxy. The quasi-unidirectional harakeke fibres enhanced both the tensile and flexural

strength of neat resin by 25% and 32%, respectively, whilst short harakeke fibres did not affect significantly the flexural strength, indeed they caused a decrease of tensile strength by around 40%. The poor performance of the short fibre composites was considered due to the poor fibre alignment and the weakness of fibre-matrix interface as confirmed by SEM and acoustic emission (AE) analysis. The addition of untreated harakeke fibres in an epoxy resin positively influenced the thermal stability of the composites.

## 2.6 Factors affecting composite properties

Natural fibre composite strength can be estimated using the modified rule of mixtures [74]

$$\sigma_c = k_1 k_2 \sigma_f V_f + \sigma_m (1 - V_f) \quad (2.1)$$

where  $k_1$  is an orientation factor,  $k_2$  is the length efficiency factor (incorporating interfacial strength),  $\sigma$  and  $V$  are average tensile strength and volume fraction, respectively, subscripts c, f and m denote composite, fibre and matrix, respectively.

Young's modulus of natural fibre composites can be also estimated using the same form of the equation with tensile strength ( $\sigma$ ) replaced by Young's modulus (E).

Looking at the equation, it can be seen that composite properties depend on fibre and matrix volume fractions, mechanical properties of the fibre and the matrix, fibre length, interfacial strength and fibre orientation. The fibres are normally much stronger and stiffer than the matrix so they would contribute to the

composite strength and stiffness much more than the matrix. Therefore, the fibre related factors are discussed further.

### **2.6.1 Fibre volume fraction**

Fibre volume fraction plays an important role in determining the composite mechanical properties. In theory, the composite mechanical properties increase as fibre volume fraction increases. In practice, this relies on having reasonable fibre/matrix interfacial strength, and strength can reduce with strongly hydrophobic matrices such as polypropylene (PP) with increasing fibre content unless coupling agents or some other interfacial engineering method is used; regardless, Young's modulus still generally increases with fibre content but more modestly than when the interface is not optimised [75]. At very high fibre content, the wetting of the fibres with the polymer matrix is insufficient, leading to a reduction of the composite strength. The strength of kenaf/PLA composites, for example, has been found to increase linearly with an increase in fibre volume fraction up to 0.7, after which a reduction in strength was observed [76].

The decrease in composite mechanical properties at high fibre volume fractions is also considered to occur due to fibre breakage during composite processing [77]. During the manufacture of short fibre reinforced polymers using injection moulding, fibres can be broken due to fibre-polymer interactions, fibre-fibre interactions, and fibre contact with the surfaces of the processing equipment which are increased at high fibre volume fractions, resulting in a reduction in the mean fibre length, and if the mean fibre length is below the critical fibre length, the reinforcement efficiency is much reduced.

### 2.6.2 Fibre length

Fibre length, which can be incorporated into the aspect ratio for a fibre (length/diameter), is an important factor influencing the mechanical properties of composites. In a short fibre composite, tensile stress is transferred from the matrix to the fibre through shear at the fibre/matrix interface. The stress is zero at the ends of the fibre and increases along the fibre length; therefore, a fibre needs to have a length greater than a critical length ( $L_c$ ) in order for the fibre to be able to be broken during tensile loading of a composite [1].  $L_c$  can be expressed as follows:

$$L_c = \sigma_f (D/2\tau) \quad (2.2)$$

where  $\sigma_f$  is tensile strength of the fibre,  $D$  is fibre diameter and  $\tau$  is the interfacial strength.

As seen in Equation 2.2, the critical fibre length is not only determined by fibre properties (strength and length), but also by the quality of the fibre/matrix interface. A fibre much shorter than the critical fibre length will not make a significant contribution to composite strength, as it will be pulled out of the matrix, before it can be fully stressed. In contrast, a fibre longer than the critical fibre length has a much greater proportion of the fibre that can be fully stressed, and can therefore contribute more to composite strength. At critical length, a fibre can be fully stressed, but only at a very small location in the middle of the fibre.

Longer reinforcing fibres are thus more desirable in a composite material, but for some process of short fibre composites such as injection moulding, if the fibre aspect ratio is too high, the fibres may get entangled during processing, resulting

in poor fibre dispersion. An aspect ratio in the range of 100 – 200 after composite processing is recommended for high performance short-fibre reinforced composites.

### **2.6.3 Fibre/matrix interfacial bonding**

Interfacial bonding largely depends on the adhesion between the reinforcement and the matrix. The adhesion plays an important role to transfer the stress from the matrix to the fibre and thus contributes towards the properties of the composites. Bonding may occur when there is an intimate contact through wetting of the reinforcement with the matrix. A number of different types of bond may be formed, including:

- Mechanical bonding: a mechanical interlocking or keying of two surfaces.
- Electrostatic bonding: occurs between two surfaces when one surface is positively charged and the other negatively charged.
- Chemical bonding: formed between chemical groups on the reinforcement surface and groups in the matrix.
- Reaction or inter-diffusion bonding: formed due to the atoms or molecules of two constituents of the composite inter-diffusing at the surface.

Insufficient wetting, resulting in poor surface adhesion, is the principal reason for the formation of a weak or ineffective interface between the fibre and the matrix. Most thermoplastics (e.g. PP and PE) are generally non-polar (hydrophobic) in nature, which makes them incompatible with polar (hydrophilic) natural fibres and thus results in an inefficient fibre matrix bonding. On the other hand,

thermosets like epoxy and phenolic are known to be able to form covalent cross-links with plant cell walls via -OH groups [78].

In terms of mathematics, the bonding influences the composite mechanical properties via factor  $k_2$  in Equation 2.1, which can be determined by:

$$k_2 = L/2L_c \text{ for } L < L_c \quad (2.3)$$

or

$$k_2 = 1 - (L_c/2L) \text{ for } L > L_c \quad (2.4)$$

where  $L$  is fibre length

When interfacial bonding is improved meaning that the interfacial shear strength ( $\tau$ ) will be increased, there will be a reduction of the critical fibre length ( $L_c$ ). Looking at Equations 2.3 and 2.4, decreased  $L_c$  leads an increase of  $k_2$ , and therefore increase the mechanical properties of composites.

It has been found that physical treatment and chemical treatments can improve interfacial bonding of natural fibre composites [79-81].

#### **2.6.4 Fibre orientation**

As be seen in Equation 2.1, fibre orientation is an important parameter that affects the mechanical properties of composites including natural short fibre reinforced composites. Reinforcing fibres aligned parallel to the direction of the applied load provide the greatest composite strength and stiffness. Long natural fibre can be easily aligned by hand combing [55; 82] or hand carding machines [57; 83]. Alternatively, intermediate processing can also be conducted such as is carried out for textile fibre including spinning to produce continuous material that can then be

directionally controlled during composite manufacture, however, this requires substantial infrastructure. It is more difficult to control alignment of short fibre, although some degree of alignment can occur in processes involving material flow such as extrusion and injection moulding. Furthermore, fibre can also be damaged during such processes. Production of aligned short natural fibre mats to make composites that could be used in compression moulding with both thermoplastic and thermosetting matrices sets a challenge.

## **2.7 Hybrid biocomposites**

A hybrid composite is a composite which has two or more different types of fibres incorporated into a common matrix. In principle, several different types of fibres can be incorporated into a hybrid system but in practice it is likely that a hybrid composition of only two types of fibres would be most common [2]. There are several types of hybrid composites. According to the manner which fibres are incorporated, hybrid composites are classified into:

- Sandwich hybrids: one fibre material (core) is sandwiched by two layers of another (shell). This type is also referred as a core-shell hybrid.
- Interply hybrids: layers of two or more fibre materials are configured alternately.
- Intraply hybrids: tows of two or more fibre materials are incorporated in a regular or random manner.
- Intimately mixed hybrids: different types of fibre are interdispersed.
- Other types such as hybrids with reinforcement using ribs, thin veils of fibre and combinations of the above types.



By mingling two or more types of fibre in a resin to form a hybrid composite it may be possible to produce a material having the combined benefits of the individual components and simultaneously moderating their less desirable qualities. Furthermore, it is possible to tailor the properties of such materials to suit specific requirements [2]. A combination of carbon and glass fibres [2-4] used in the same polymeric matrix to create hybrids is a typical instance. Carbon fibre provides strong, stiff and low density reinforcement but is relatively expensive and brittle, whilst glass fibre is relatively cheap and tougher but its strength and stiffness are relatively disadvantageous. By combining the two types of fibre within the same matrix, it may be possible to achieve a balance between the properties of all-carbon fibre reinforced plastic and all-glass fibre reinforced [4].

Further, synergy described as “the hybrid effect” has been obtained for hybrid composites. Some people consider a positive deviation of a certain property from rule of mixtures as the hybrid effect, whilst others define the hybrid effect as the enhancement of the failure strain of the lower elongation reinforcement when part of a hybrid composite [46]. The latter is the initial and basic definition. The first observation of this phenomenon is generally credited to Hayashi [3], and then different works have been carried out to prove and verify existence of this effect [46]. Initially, the hybrid effect had been observed on hybrid composites of carbon fibre and other synthetic fibres such as glass and Kevlar. Among these works, Zweben’s [84], Bunsell and Harris’ [2], and Fukuda’s [85] are typical examples. In the 21<sup>st</sup> century, a variety of works has looked at either combination of glass fibre and natural fibres in hybrid composites [59; 82; 86-92] or combination of different types of natural fibre (hybrid biocomposites) [93-107].

The focus when combining two natural fibres has been generally on obtaining a better balance in mechanical, chemical and physical properties, rather than on optimising the hybrid effect. Another reason is that research in natural fibre composites often deals with random mats and short fibres, which make hybrid effects more difficult to find [11].

In this project, aligned long and short harakeke and hemp fibre were combined and it was assessed whether the hybrid effect occurs.

## **Chapter Three: Fibre treatment and characterisation**

### **3.1 Introduction**

This chapter reports the following results:

- Fibre morphology
- Fibre lumen volume fraction
- Fibre physical and mechanical properties

### **3.2 Experimental**

#### **3.2.1 Materials**

Long fibre bundles mechanically extracted from harakeke leaves were obtained from the Templeton Flax Mill, Riverton, New Zealand. Retted hemp bast fibre was supplied by Hemcore, UK.

Analytical grade  $\text{Na}_2\text{SO}_3$  and NaOH pellets with 98% purity supplied by Sigma Aldrich were used to treat the fibres.

#### **3.2.2 Methods**

##### ***3.2.2.1 Preparation of Alkali solution***

Alkali treatment is commonly used in the pulp and paper industries to separate fibre bundles into elementary fibres and eliminates lignin and other non-fibrous components from fibres. This method can be also used to pulp hemp fibre and harakeke fibre.

### **NaOH treatment**

In order to treat a 70g sample of harakeke fibre with the required alkali solution concentration (2%) and fibre: liquor ratio (1:8), 11.2 g analytical grade NaOH (98% purity) was dissolved in 548.8 ml water and added to the pre-weighed quantity of fibre.

### **NaOH/Na<sub>2</sub>SO<sub>3</sub> treatment**

In order to treat a 70g sample of harakeke or hemp fibre with the required alkali solution concentration (5%NaOH/2%Na<sub>2</sub>SO<sub>3</sub>) and fibre: liquor ratio (1:8), 28g analytical grade NaOH (98% purity) and 11.2g Na<sub>2</sub>SO<sub>3</sub> was dissolved in 520.8ml water and added to the pre-weighed quantity of fibre

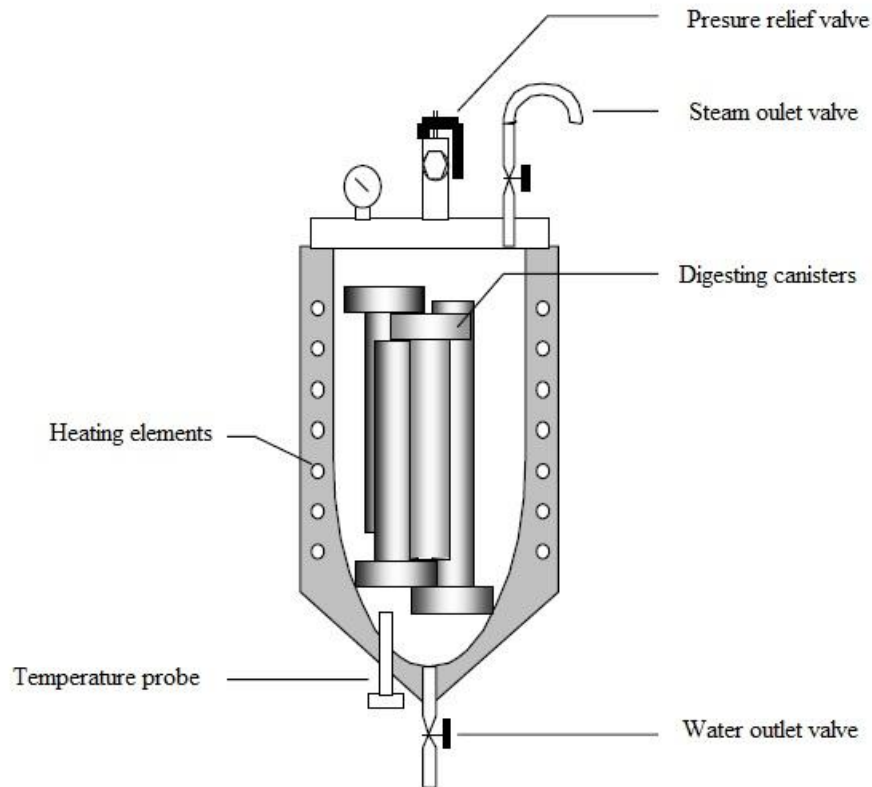
#### ***3.2.2.2 Fibre pulping***

Fibre pulping was conducted to remove unwanted fibre components and to break down fibre bundles into finer bundles and even single fibres (individual cells). Harakeke fibre bundles and retted hemp fibres were initially granulated using a mesh with holes of diameter 4 mm and then pulped using a laboratory scale pulp digester Figure 3.1.

#### ***3.2.2.3 Fibre length, cell wall thickness and diameter measurement***

Fibre length, fibre cell wall thickness and diameter were measured using a Kajaani Fibrelab electronic sequential fibre analyser. Two samples of approximately 6000 fibres were analysed and a mean fibre length, diameter, cell wall thickness and fibre length distribution were reported. A few long and (or) coarse fibres which could block the analyser were removed from the sample using tweezers so actual fibre length and diameter could be slightly higher than from

those analysed, however, due to the huge number of fibres measured, the difference was assumed negligible.



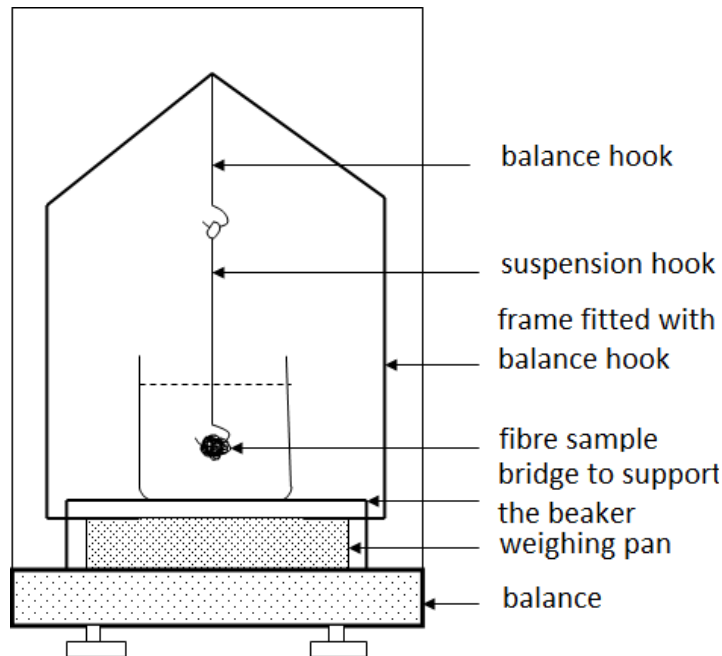
**Figure 3.1: Schematic of a pulp digester [51].**

#### **3.2.2.4 Fibre density measurement**

Natural fibre density can be measured by one of five methods: (1) diameter and linear density, (2) Archimedes, (3) helium pycnometry, (4) gradient column and (5) liquid pycnometry. From these, Archimedes using canola oil as an immersion fluid was adopted here because it is simple, quick to give the test results and bears the lowest cost [108]. Testing was based on ASTM D3800-99 (Standard Test Method for Density of High-Modulus Fibers) using the apparatus as shown in Figure 3.2. Three specimens of harakeke fibre bundles weighing about 1 g were

oven dried at 60° C for 72 hours and then placed in a vacuum oven at room temperature for 5 minutes to remove trapped air between fibre cells before testing.

The average density was calculated.



**Figure 3.2: Schematic diagram of apparatus for density measurement.**

### **3.2.2.5 Determining lumen volume fraction**

Pulped fibres (single fibres) treated with 5%NaOH/2%Na<sub>2</sub>SO<sub>3</sub>were used to determine single fibre diameter and fibre wall thickness using a Kajaani Fibrelab electronic sequential fibre analyser. Approximately 6000 fibres were analysed and a mean fibre diameter and fibre wall thickness were determined. Assuming that fibre lumen and single fibre cross sections are circular and consistent along the fibre length, lumen diameter would be:

$$D_l = D_{sf} - 2T_w \quad (3.1)$$

where  $D_l$ ,  $D_f$  and  $T_w$  are average lumen diameter, fibre diameter and fibre wall thickness, respectively and

average lumen volume fraction in single fibres would be:

$$V_l = v_l/v_{sf} = A_l/A_{sf} \quad (3.2)$$

and average lumen volume fraction in fibre bundles would be:

$$V'_l = v_l/v_{fb} \quad (3.3)$$

where  $v$  is volume and  $A$  is cross sectional area; subscripts  $l$ ,  $sf$  and  $fb$  denotes lumen, single fibre and fibre bundle, respectively.

Combination of (3.2) and (3.3) leads to:

$$V'_l = V_l(v_{sf}/v_{fb}) = V_l(m_{sf}/m_{fb})(\rho_{fb}/\rho_{sf}) \quad (3.4)$$

where:

$$Y_p = m_{sf}/m_{fb} \quad (3.5)$$

and  $Y_p$  is the pulp yield;  $m_{sf}$  and  $m_{fb}$  are the mass of oven-dried single fibres (pulped fibres) and fibre bundles, respectively;  $\rho$  is density.

#### **3.2.2.6 Single fibre tensile testing**

Single fibre tensile testing was based on ASTM C 1557-03 (Standard Test Method for Tensile Strength and Young's Modulus of Fibers). Thirty untreated or treated elementary (single) fibres were mounted on 2 mm thick cardboard with a 2 mm length window that set the fibre gauge length as shown in Figure 3.3. The two ends of each fibre were glued to the cardboard using cyanoacrylate glue. Mounted

fibres were observed using an Olympus BX60F5 microscope to make sure they were single. Fibres were assumed perfectly circular. Diameters of selected fibres were measured at 3 points along the fibre length under the same microscope with a magnification of 200 and the average diameter was calculated and used for calculation of tensile properties. The cardboard windows with single mounted fibres were then individually placed in the grips of an Instron 4204 tensile testing machine fitted with a 10 N-load cell, and the supporting sides of the cards were carefully cut using a hot wire cutter. The fibres were tensile tested to failure at a rate of 0.5 mm/min. Average fibre tensile strength and Young's modulus and failure strain were obtained using the results from thirty specimens.

Fibres with small diameter do not allow the attachment of an extensometer for measuring the displacement (elongation) of the fibre so fibre elongation can only be measured from the cross-head displacement of the tensile tester. However, the cross-head displacement is the combination of the fibre elongation as well as cross-head, specimen gripping system and specimen mounting card deformation. Therefore, it is necessary to determine the system compliance ( $C_s$ ) for correcting the fibre elongation. The system compliance was determined experimentally using the guide from the standard ASTM C 1557-03.

The cross-head displacement  $\Delta L$  (mm) can be expressed by:

$$\Delta L/F = (1/EA)l_o + C_s \quad (3.6)$$

Where,  $l_o$  is the specimen gauge length (mm),  $E$  is the Young's modulus of the fibre (MPa),  $A$  is the cross-sectional area of the fibre ( $\text{mm}^2$ ) and  $F$  is the applied force (N). Therefore, the plot of  $\Delta L/F$  (which can be determined from the force



versus cross-head displacement curve of the fibre) versus  $l_0$  will yields a straight line with slope of  $1/EA$  and intercept  $C_s$  which is the value of system compliance.

The actual fibre elongation  $\Delta l$  (mm) can be determined by:

$$\Delta l = \Delta L - C_s F \quad (3.7)$$

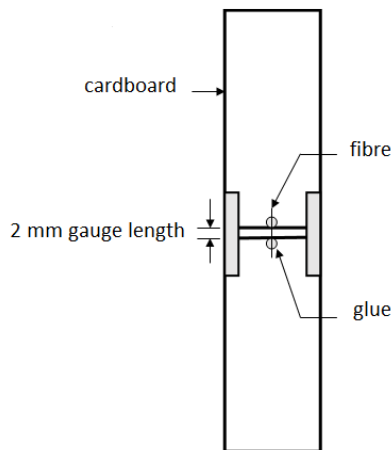
And the fibre strain will be:

$$\varepsilon = \Delta l / l_0 \quad (3.8)$$

The fibre stress  $\sigma$  (MPa) is expressed by:

$$\sigma = F_{max} / A \quad (3.9)$$

Where,  $F_{max}$  is the maximum applied force (N). Equations (3.2), (3.3) and (3.4) were utilised with digital data recorded during tensile testing to produce the actual stress versus strain curve of each specimen. The Young's modulus was determined from the slope of the linear section of the curve. The failure strain was the strain corresponding to maximum force.



**Figure 3.3: Schematic diagram of cardboard with a mounted single fibre used in single fibre testing.**

### **3.2.2.7 Microscopy**

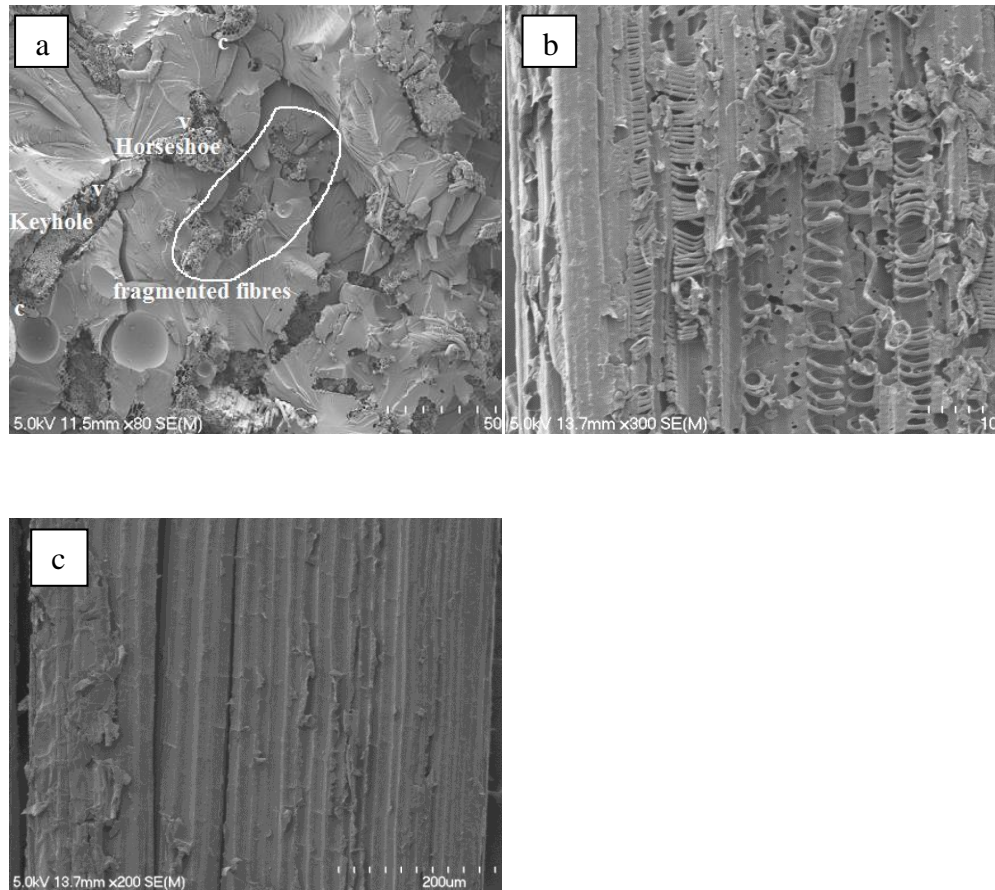
An optical light microscope Olympus BX60F5 was used to determine if fibres are single and measure fibre diameter for single fibre tensile testing. Fibre surfaces were investigated using a Hitachi S4100 field emission scanning electron microscope (FESEM) operated at 5 kV. All samples were mounted on aluminium stubs using carbon tape and then sputter coated with platinum to make them conductive prior to observation.

## **3.3 Results and discussion**

### **3.3.1 Fibre morphology**

In harakeke leaves, fibre bundles have different cross sectional shapes including “key-holes” and “horseshoes” or “molar teeth” [56; 57; 109-111]. The “key-hole” bundles which have larger cross section are located in the upper part of the leaf while the “horseshoe” bundles are in the lower part and between these bundles, in the centre of the leaf are helical fibril cells with a thin wall called vascular bundles which are considered to be the pathways of fluids in the leaf [56; 110]. The fibre bundles are usually surrounded by thin walled cells known as sheath cells and cuticles or epidermis still adhere to the fibre bundles at the side close to the leaf surface [56; 57]. When fibre bundles are extracted from the leaves, some of them are longitudinally split into smaller bundles [56]. Figure 3.4 shows examples of all the above features of harakeke fibre. “Key-hole” and “horseshoe” bundles and fragmented bundles are shown in Figure 3.4a and vascular bundles, sheath cells and cuticles are labelled v, s and c respectively. Figure 3.4b shows the helical

structure of vascular bundles. The surface of a harakeke fibre bundle is shown in Figure 3.4c.

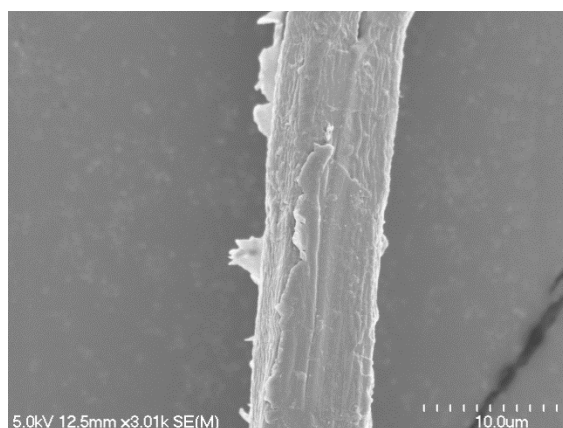


**Figure 3.4: FESEM images of harakeke fibre morphology: (a) different cross sectional shapes of fibre bundles in composites, (b) helical structure of vascular bundles seen on split as-supplied fibre bundles and (c) fibre bundle surface (as supplied).**

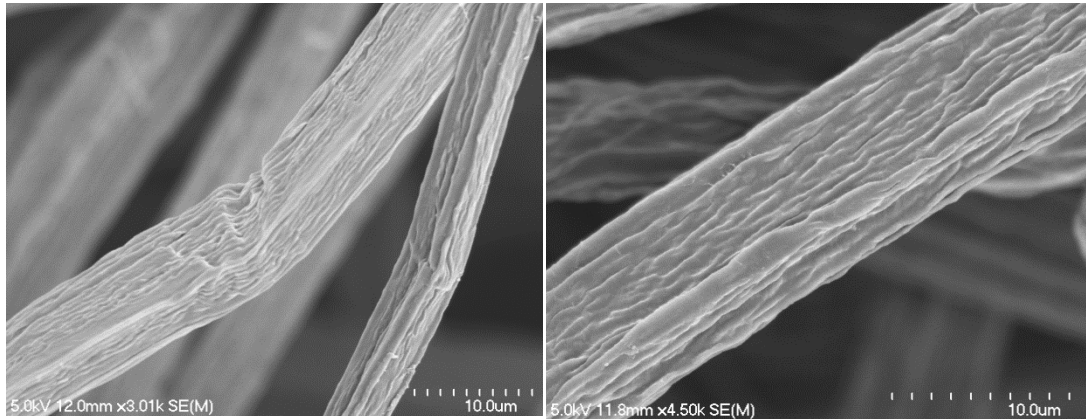
It can be seen that the surface of harakeke fibre bundles is uneven with ridges along the length of the fibre which may enhance mechanical bonding between fibre bundles and the matrix. However, non-cellulose compounds such as waxes or fats and surface impurities known to be present on such untreated fibre may limit bonding at the interface between fibre bundles and the polymeric matrix [110]. Long harakeke fibre bundles extracted from the harakeke plant leaves contain single fibres (also called individual / elementary fibres / ultimate fibres).

The single fibre has a polygonal cross-section with a central lumen surrounding by a thick wall and their length varies from 3.7-5.2 mm and the diameter is approximately 10 – 15  $\mu\text{m}$  [57; 62; 112].

The surface of a untreated individual harakeke fibre, which was manually extracted from the fibre bundle, is shown in Figure 3.5 and NaOH treated and NaOH/ $\text{Na}_2\text{SO}_3$  treated individual harakeke fibres can be seen in Figure 3.6 (a) and 3.6 (b). It can be observed clearly that components known including lignin, pectin and wax are adhered to the surface of untreated fibre. In contrast, NaOH and NaOH/ $\text{Na}_2\text{SO}_3$  treated fibres reveal rough surfaces with large numbers of striations which might enhance the fibre-matrix bonding. There seems to be no difference between the surfaces of two types of the treated single fibres.

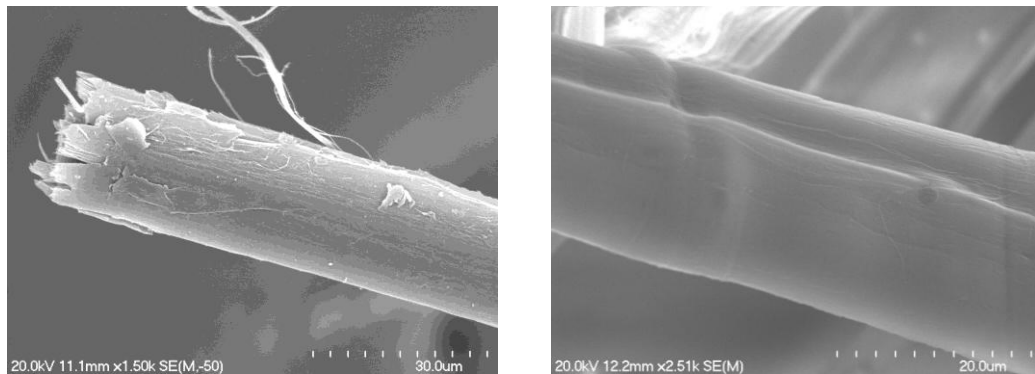


**Figure 3.5: SEM image of untreated harakeke single fibre surface.**



**Figure 3.6: SEM images of treated single fibres: (a) NaOH treated and (b) NaOH/Na<sub>2</sub>SO<sub>3</sub> treated.**

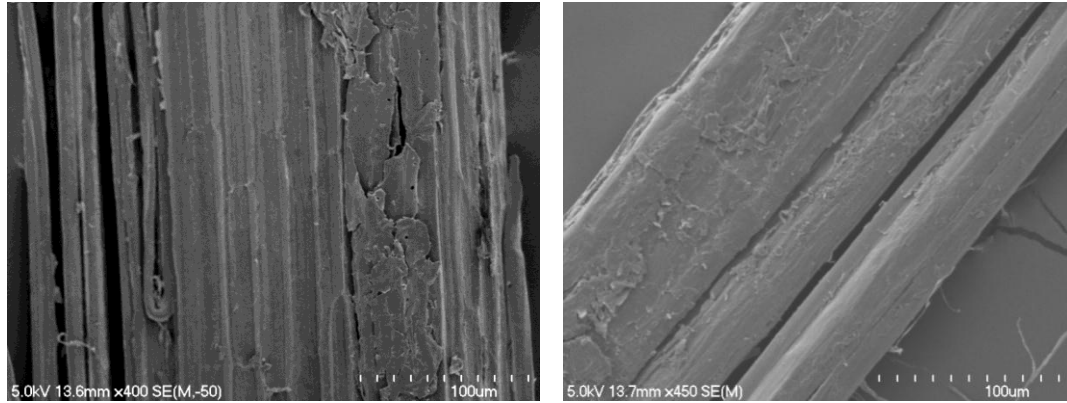
Likewise for hemp, NaOH/Na<sub>2</sub>SO<sub>3</sub> showed the efficiency in fibre surface treatment removing lignin, pectin and wax as shown in Figure 3.7. However, the surface of treated hemp was less rugose than that of treated harakeke.



**Figure 3.7: SEM images of single hemp fibres: (a) untreated and (b) NaOH/NaOH/Na<sub>2</sub>SO<sub>3</sub> treated.**

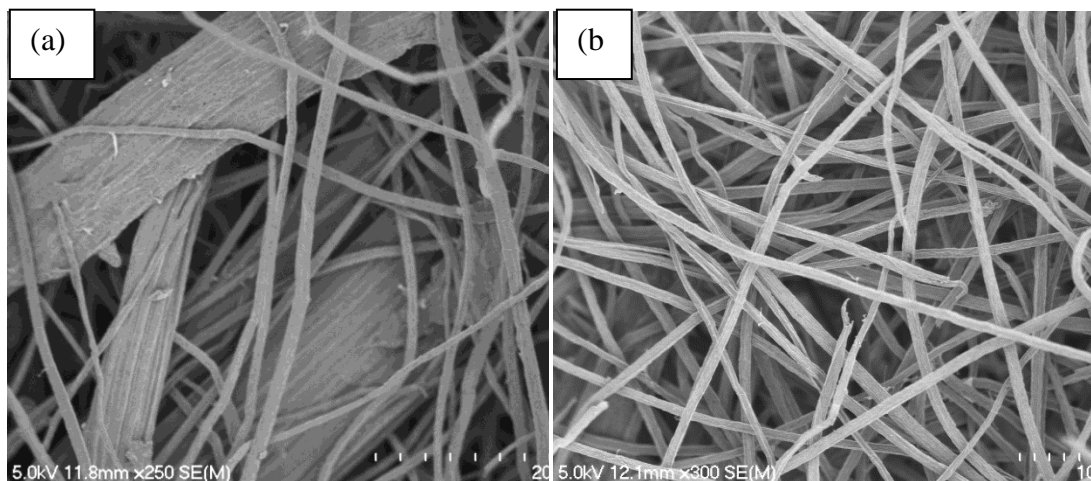
### 3.3.2 Fibre separation

As mentioned previously, fibre pulping breaks down harakeke or hemp fibre bundles (Figure 3.8) into single fibres.

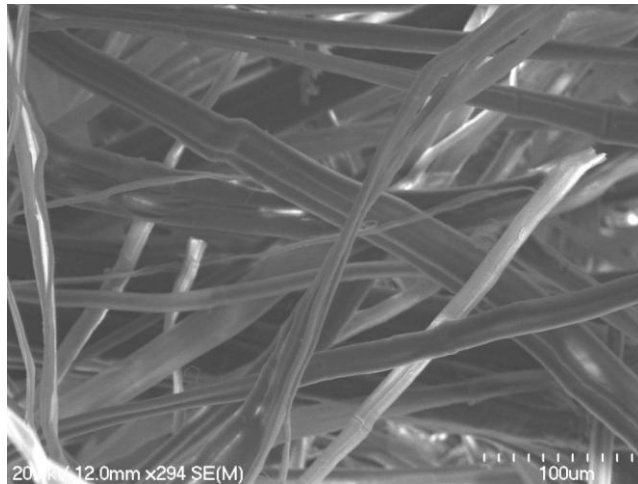


**Figure 3.8: SEM images of untreated fibre bundles: (a) harakeke and (b) hemp.**

With 2% NaOH treatment, not all harakeke fibres were separated into single fibres and there were some fibre bundles remaining (Figure 3.9a) while 5%NaOH/2%Na<sub>2</sub>SO<sub>3</sub> treated fibres were almost separated into single fibres (Figure 3.9b). This was expected as 5%NaOH/2%Na<sub>2</sub>SO<sub>3</sub> treatment with higher concentration of NaOH and support of Na<sub>2</sub>SO<sub>3</sub> removes the lignin and pectin, which bind individual fibres together, more effectively than 2%NaOH treatment. Likewise for hemp, treated hemp fibre was well separated as shown in Figure 3.10.



**Figure 3.9: SEM images of treated harakeke fibre mats showing fibre separation: (a) NaOH treated and (b) NaOH/Na<sub>2</sub>SO<sub>3</sub> treated.**

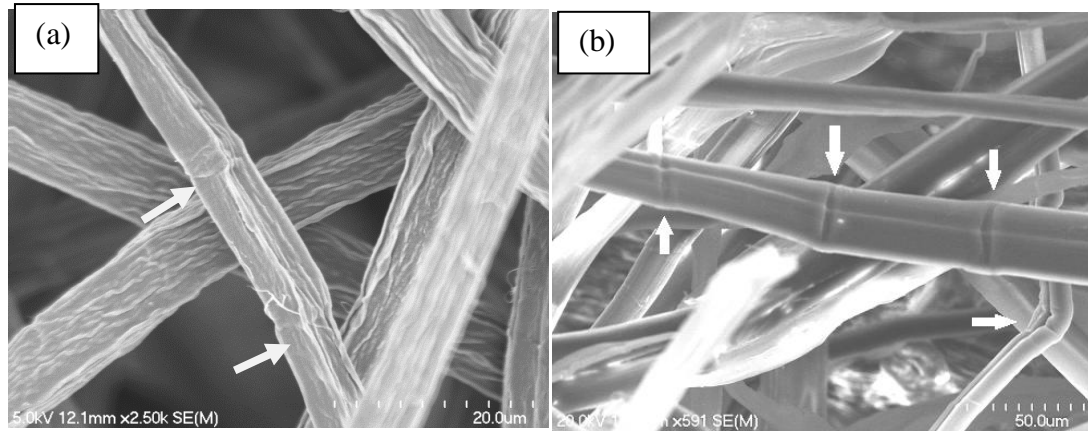


**Figure 3.10: SEM image of treated hemp fibre mats showing fibre separation.**

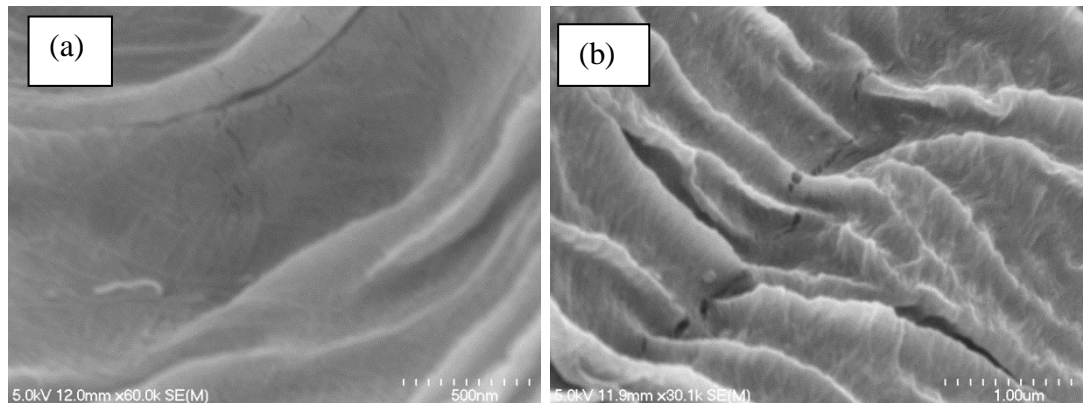
### **3.3.3 Fibre defects**

Figure 3.11 shows kink bands [45] of harakeke and hemp, naturally occurring fibre defects marked by arrows. However, the number of kink bands observed on pulped harakeke fibres was very small compared to the numbers that have seen in other work on flax fibre [45; 91; 92; 113] and hemp fibre [90]. These are believed to be due to the change of microfibril angle relative to the fibre axis at the defect region leading to the change of crystalline orientation [90] and act as a region of weakness in the fibre. These defects weaken fibres and could affect the mechanical properties of composites. At the side of the harakeke kink bands, micro-cracks on the surface were observed. The micro-cracks were more common and clearer on the surfaces of 5%NaOH/2%Na<sub>2</sub>SO<sub>3</sub> treated harakeke fibre than those of 2%NaOH treated harakeke fibre as shown in Figure 3.12. Micro-cracks on 2%NaOH treated fibre appeared when captured at very high magnification (about 60.000 times) while those on 5%NaOH/2%Na<sub>2</sub>SO<sub>3</sub> were much clearer at much lower magnification (about 30.000 times). Figure 3.13

shows fibres with micro-holes which appear occasionally. These holes may be the consequence of diseased leaves.

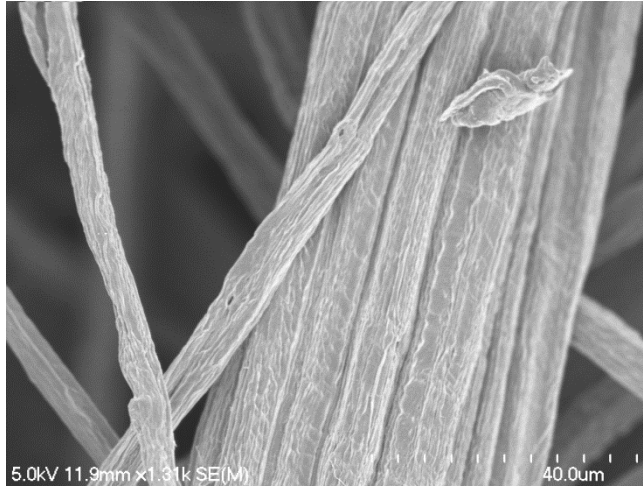


**Figure 3.11: SEM images of single fibres with kink bands marked by arrows in a pulped fibre mats: (a) harakeke (b) hemp.**



**Figure 3.12: SEM images of micro-crack on the surfaces of treated harakeke fibres at the location of kink bands: (a) NaOH treated and (b) NaOH/Na<sub>2</sub>SO<sub>3</sub> treated.**





**Figure 3.13: SEM image of treated harakeke fibre with micro-holes.**

### **3.3.4 Fibre lumen fraction**

Physical properties of 5%NaOH/2%Na<sub>2</sub>SO<sub>3</sub> treated harakeke and hemp fibres obtained using a Kajaani Fibrelab are summarised in Table 3.1. Lumen diameter was calculated from fibre cell wall thickness using Equation 3.1. A single fibre and its lumen were assumed perfectly circular so the area fraction of fibre wall thickness cross-section would be equal to  $1 - (D_l/D_f)^2$ , called correcting factor. Tensile strength and Young's modulus were corrected by dividing their tested values by a correcting factor. This manner of correcting tensile strength and Young's modulus has been applied for harakeke fibre [109]. The fibre lumen fractions which were calculated based on fibre lumen diameters, cell wall thicknesses, single fibre diameters and fibre pulp yields using Equation 3.4 are presented in Table 3.1.

Lumen fractions of harakeke were compared with and hemp and other plant fibres in Table 3.2. It can be seen that harakeke lumen fraction was similar to sisal and jute but significantly higher than hemp and flax fibres. The high lumen fraction of

harakeke fibres was expected to significantly contribute to harakeke composite porosity.

**Table 3.1: Physical properties of harakeke and hemp fibres.**

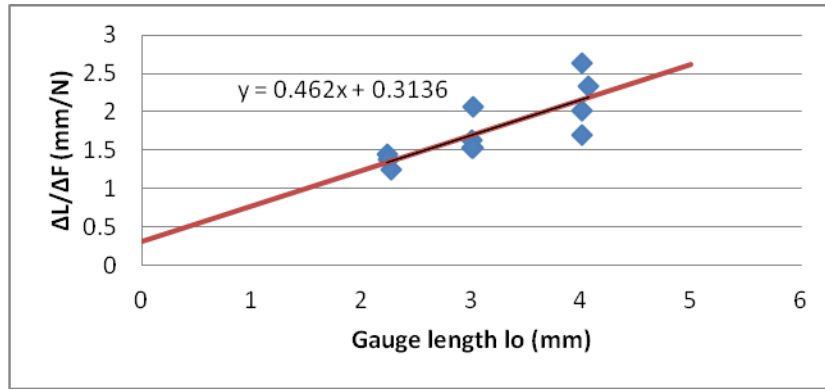
Fibre	Density (g/cm <sup>3</sup> )	Fibre diameter (μ)	Wall thickness (μ)	Lumen diameter (μ)	Pulp yield	Lumen fraction V <sub>l</sub>	Lumen fraction V' <sub>l</sub>	Corrected factor
Harakeke	1.523	14.98	2.72	9.54	0.43	0.41	0.21	0.59
Hemp	1.522	21.55	6.16	9.23	0.61	0.18	0.11	0.82

**Table 3.2: Comparison of lumen diameter, cell wall thickness and lumen fraction of harakeke and hemp fibres with some other plant fibres.**

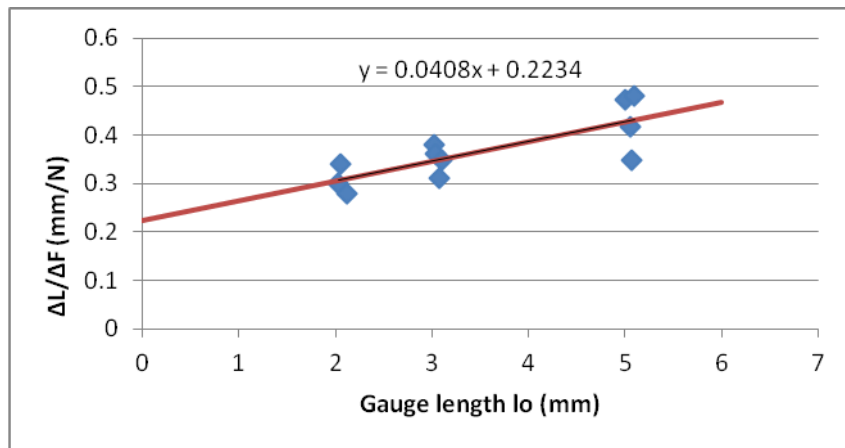
Fibre	Flax [114]	Jute [115]	Sisal [115]	Hemp	Harakeke
Lumen diameter (μm)	5	6.7	8.2	9.23	9.54
Cell wall thickness (μm)	-	2.5	2.6	6.16	2.72
Lumen fraction	0.068	0.254	0.252	0.110	0.214

### 3.3.5 Physical and mechanical properties of fibres

The system compliances of the tensile testing system for harakeke and hemp fibres were determined using gauge lengths of single fibres of 2, 3 and 4 mm for harakeke fibre and 2, 3 and 5 mm for hemp fibre shown in Figure 3.14 and Figure 3.15, respectively. Comparison of the best fit equations  $y = 0.462x + 0.3136$  for harakeke and  $y = 0.0408x + 0.2234$  for hemp to Equation 3.5, where  $y$  is  $\Delta L/F$  and  $x$  is gauge length gives the value of the system compliance  $C_s = 0.3136$  for harakeke fibre and 0.2234 for hemp fibre as the intercepts with the y-axis.



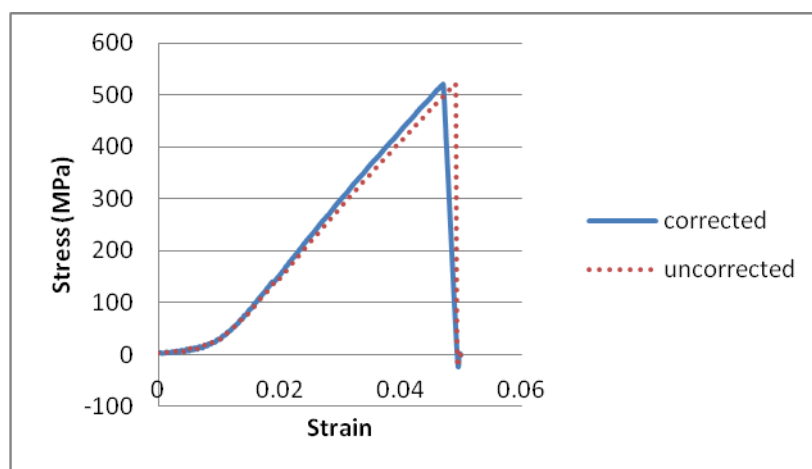
**Figure 3.14: Graph based on Equation 3.5 to obtain system compliance of the tensile testing system for harakeke fibre.**



**Figure 3.15: Graph based on Equation 3.5 to obtain system compliance of the tensile testing system for hemp fibre.**

The system compliance values were applied to correct the fibre elongation and produce stress-strain curves for each specimen, an example of which is shown in Figure. 3.16. It can be seen that the stress-strain curves of the fibres moved to the left on applying the system compliance such that failure strain would reduce and Young's modulus would increase relative to uncorrected values. A typical stress-strain graph for harakeke fibre (see Figure 3.16) had an initial non-linear portion which was attributed to the orientation of the fibrils along the axis of the fibre under load [116]. With higher loading, the fibre response became linear and this

linear portion was used for Young's modulus determination using a linear regression equation fitted to the data.



**Figure 3.16: Typical stress vs strain curves of harakeke fibre uncorrected based on crosshead motion and corrected using  $C_s$ .**

The physical and mechanical properties of harakeke and hemp fibres are tabulated in Table 3.3 and Table 3.4, respectively, with the values in the brackets being standard deviation.

It can be seen that untreated harakeke density ( $1.27 \text{ g/cm}^3$ ) is significantly lower than density of hemp and other fibres (see Table 2.4) while the tensile strength (778 MPa) and Young's modulus (32.09 GPa) are comparable to those for other fibres (see Table 2.4). This suggests that harakeke fibre could contribute to higher specific mechanical properties of composites. Densities of harakeke and hemp increased after the treatments. It may be due to the elimination of amorphous materials off from the fibres [117]. Moreover, a positive change in fibre densities normally signifies cell wall densification [118]. Diameters of harakeke and hemp fibres remained after treatment. This was confirmed by statistic analysis using one-tailed Student's t-test at a confidence level of 95% ( $P < 0.05$ ).

**Table 3.3: Physical and mechanical properties of harakeke fibres.**

Treatment	Diameter ( $\mu$ )	Density (g/cm <sup>3</sup> )	Max Load (N)	Tensile strength (MPa)	Youngs modulus (GPa)	Failure strain (%)
Untreated	13.37 (4.92)	1.274 (0.016)	0.092 (0.046)	778 (471)	32.1 (22.2)	4.54 (1.96)
NaOH	12.84 (1.91)	1.515 (0.026)	0.094 (0.028)	756 (244)	28.1 (15.6)	6.24 (2.19)
NaOH/Na <sub>2</sub> SO <sub>3</sub>	12.38 (2.15)	1.523 (0.035)	0.071 (0.029)	579 (193)	21.7 (11.4)	6.25 (2.06)

**Table 3.4: Physical and mechanical properties of hemp fibres.**

Treatment	Diameter ( $\mu$ )	Density (g/cm <sup>3</sup> )	Max Load (N)	Tensile strength (MPa)	Youngs modulus (GPa)	Failure strain (%)
Untreated	20.82 (6.33)	1.501 (0.013)	0.204 (0.15)	621 (355)	33.2 (20.8)	3.29 (1.52)
NaOH/Na <sub>2</sub> SO <sub>3</sub>	21.49 (4.75)	1.522 (0.049)	0.192 (0.119)	591 (371)	34.1 (19.7)	4.72 (2.05)

When looking at the average values in Table 3.3, NaOH and NaOH/Na<sub>2</sub>SO<sub>3</sub> treatments appeared to reduce tensile strength and Young's modulus of treated harakeke fibres in relation to those of untreated fibre. The data was statistically analysed using a one-tailed Student's t-test at a confidence level of 95% ( $P < 0.05$ ) to determine the significance of the difference in the fibre tensile strength and Young's modulus of each of the fibre treatments in relation to that of the control (untreated fibre). According to the Student's t-test results, there are no significant increases in fibre tensile strength and Young's modulus of NaOH treated harakeke fibres when compared to the control, although the averaged test results suggest that the tensile strength and Young's modulus of the NaOH treated fibres are

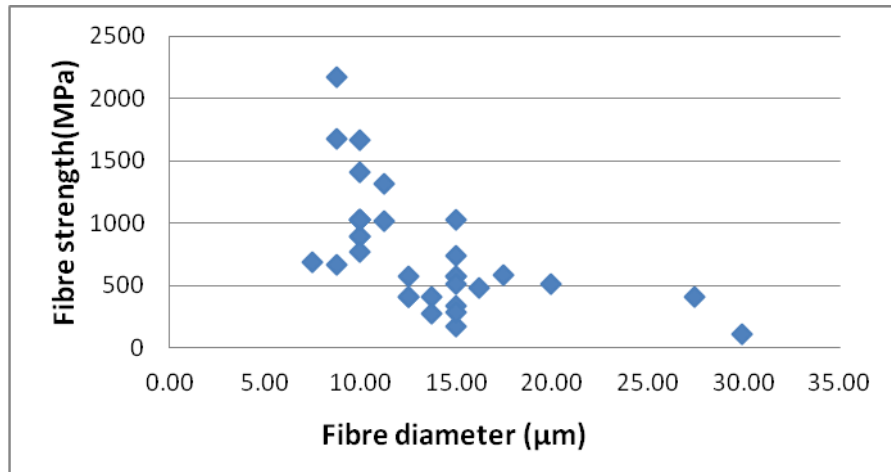
slightly junior. The Student's t-test results also indicate that there are significant decreases in tensile strength and Young's modulus of NaOH/Na<sub>2</sub>SO<sub>3</sub> treated fibres when compared to the control. It can thus be seen that the NaOH fibre treatment did not dramatically affect the tensile strength and Young's modulus of harakeke fibres, suggesting that no degradation occurred to the cellulose microfibrils during the alkali treatment. The NaOH/Na<sub>2</sub>SO<sub>3</sub> treatment, however, resulted in a significant reduction in harakeke fibre strength and Young's modulus as a result of cellulose degradation, which is often associated with treatments involving the use of high NaOH concentrations [119]. In contrast, the NaOH/Na<sub>2</sub>SO<sub>3</sub> treatment did not affect tensile strength and Young's modulus of hemp fibre which was confirmed by the one-tailed Student's t-test.

Calculation of tensile strength and Young's modulus properties is generally based on the total cross-section of a fibre or fibre bundle, however, single fibres have a central hollow lumen which takes up a significant proportion of the cross-sectional area as discussed in Section 3.3.4. Hence, it could be considered that measurements of strength and stiffness obtained not taking this into account are underestimations to the same degree. Looking back into Table 3.1, it can be seen that the lumen area fractions for single harakeke and hemp fibres were 0.41 and 0.18, respectively, giving fibre cell wall area fractions of 0.59 and 0.82, respectively. The true cross sectional areas of fibre areas excluding fibre lumens were obtained by multiplying measured fibre cross sectional area with 0.59 and 0.82 for harakeke and hemp, respectively. Tensile strength and Young's modulus of harakeke and hemp fibres were corrected accordingly and are tabulated in Table 3.5.

**Table 3.5: Corrected mechanical properties of harakeke and hemp fibres**

<b>Fibre</b>	<b>Treatment</b>	<b>Corrected tensile strength (MPa)</b>	<b>Corrected Young's modulus (GPa)</b>
<b>Harakeke</b>	Untreated	1319	54.4
	NaOH	1281	47.6
	NaOH/Na <sub>2</sub> SO <sub>3</sub>	981	36.8
<b>Hemp</b>	Untreated	757	40.5
	NaOH/Na <sub>2</sub> SO <sub>3</sub>	721	41.6

In Figure 3.17, the tensile strength values of harakeke individual fibres were plotted as a function of their diameter. It shows a decrease of tensile strength as diameter increases. This trend has been reported for other natural fibres [58; 120-122]. The wide scatter of tensile strength values is a typical drawback of natural fibres which can result in variability of composite properties.

**Figure 3.17: Single fibre strength versus fibre diameter.**

### 3.4 Chapter conclusions

Thermal-alkali treatments with 2%NaOH or 5%NaOH/2%Na<sub>2</sub>SO<sub>3</sub> for harakeke fibre and 5%NaOH/2%Na<sub>2</sub>SO<sub>3</sub> for hemp fibre were found to separate fibre bundles into finer bundles and even single fibres. Fibre densities were found to increase after treatments whilst fibre diameter was retained. The NaOH treatment for harakeke fibre and NaOH/Na<sub>2</sub>SO<sub>3</sub> treatment for hemp fibre were found not to reduce the fibre tensile strength and Young's modulus whilst NaOH/Na<sub>2</sub>SO<sub>3</sub> treatment for harakeke fibre was found to reduce the fibre tensile strength and Young's modulus considerably.

Fibre lumens were found to take up a significant proportion of the cross-sectional area with 41% and 18% for single harakeke and hemp fibres, respectively and should be taken into account as measuring strength and stiffness of the fibres to avoid underestimation. High lumen fractions were also expected to contribute considerably to porosity in composites.

SEM images of harakeke and hemp fibre surfaces showed that the gummy polysaccharides of lignin, pectin and hemicelluloses were removed from the fibres leaving rough surfaces containing large numbers of etched striations. Surfaces of harakeke fibres were found to be rougher than those of hemp fibres. It is thought that the striations would provide enhanced mechanical interlocking with the polymer matrix.

NaOH treated harakeke fibre was used to produce aligned short harakeke/epoxy composites which are presented in Chapter 4 whilst NaOH/Na<sub>2</sub>SO<sub>3</sub> treated harakeke and hemp fibres were used to aligned short harakeke/hemp hybrid composites which is presented in Chapter 6.



## Chapter Four: Aligned short harakeke/epoxy composites

### 4.1 Introduction

Fibre orientation is an important parameter that affects the mechanical properties of composites including natural short fibre reinforced composites. Even basic models for composite strength support that alignment is a major factor determining mechanical properties, through the use of an orientation factor, including the following Modified Rule of Mixtures for composite strength [74]:

$$\sigma_c = k_1 k_2 \sigma_f V_f + \sigma_m (1 - V_f) \quad (4.1)$$

where  $k_1$  is an orientation factor;  $\sigma$  and  $V$  are average tensile strength and volume fraction, respectively; subscripts c, f and m denotes composite, fibre and matrix, respectively;  $k_2$  is the length efficiency factor (incorporating to interfacial strength).

Reinforcing fibres aligned parallel to the direction of the applied load provide the greatest composite strength. Long natural fibre can be easily aligned by hand combing [55; 82] or hand carding machines [57; 83]. Alternatively, intermediate processing can also be conducted such as that carried out for textile fibre including spinning to produce continuous material that can then be directionally controlled during composite manufacture, although this requires substantial infrastructure. It is more difficult to control alignment of short fibres, however, some degree of alignment can occur in processes involving material flow such as extrusion and injection moulding, although fibre can also be damaged during such processes. Production of aligned short natural fibre mats that could be used in

compression moulding with both thermoplastic and thermosetting matrices to make composites sets a challenge.

In this work, dynamic sheet forming, a technique normally used to make paper, was used to prepare aligned short harakeke mats. Tensile and flexural properties of epoxy matrix composites made from these mats using compression moulding were evaluated and compared with randomly oriented short harakeke fibre-epoxy composites. Orientation of fibres in composites was also quantitatively estimated.

## **4.2 Experimental**

### **4.2.1 Materials**

Harakeke fibre pulped with 2% NaOH at 170°C for 40 minutes as presented in Chapter 3 was used as the reinforcement. The matrix was a low viscosity epoxy system comprised of Nuplex resin R180 and Nuplex standard hardener H180 (mixing ratio 5:1 by weight).

### **4.2.2 Methods**

#### ***4.2.2.1 Preparation of fibre mats***

Aligned harakeke pulped fibre mats were produced using an automatic dynamic sheet former (DSF) manufactured by Canpa, Canada. The main parts of the machine include a rotating centrifugal drum with screening fabric (called wire) on the inside surface of the drum and a travelling nozzle (Figure 4.1). Water is introduced through the nozzle to build up a water wall on the wire which functions as a fibre cushion. The thickness of the water wall can be set depending on the amount of fibre desired. During operation, the traversing nozzle sprays a flow of water and fibres (called stock) onto the wire to build up a fibre layer until

the required thickness is obtained. Then the water is removed and a wet fibre web is formed on the wire.



**Figure 4.1: Centrifugal drum and nozzle of a DSF.**

In this work, 40g of pulped harakeke fibre diluted in 20 litre of water was prepared to make a fibre web. The web was oven-dried at 80°C for 24 hours and then cut into fibre mats with a size of 22 x 15 cm to fit in a compression mould. Planar random oriented harakeke pulped fibre mats were formed by hand. For this, a suspension of fibre in water was poured onto a screen with very fine holes such that fibres were deposited on the screen surface to form a wet fibre mat whilst the water ran through the screen. The mat was press-dried with paper towels and then removed and oven-dried at 80°C for 24 hours. Dried fibre mats were cut to a size of 15 x 15 cm. A fibre mat weight of 105 g/m<sup>2</sup> was determined. Mats were stored in sealed bags for later use.

#### **4.2.2.2 Fibre mat tensile testing**

The tensile testing of fibre mats was based on the Tappi standard T 404 cm-92 (Tensile breaking strength and elongation of paper and paperboard). Ten strips for each direction, longitudinal and transverse to DSF spinning direction, with size of 15 x 2 cm were cut from fibre mats and conditioned at  $23^{\circ} \pm 3^{\circ} \text{C}$  and  $50\% \pm 5\%$  relative humidity for at least 40 hours. Strips were then tensile tested using an Instron-4204 universal testing machine fitted with a 10 N load cell at a crosshead speed of 1 mm/min. Breaking load was recorded and tensile strength was calculated by dividing the breaking load by the width of the tested specimen. Average longitudinal tensile strength (LTS) and transverse tensile strength (TTS) of ten specimens were reported. In the paper industry, LTS and TTS are called machine direction strength (MD) and cross direction strength (CD), respectively, which relate to the main direction of fibre alignment on the paper making machine. The fraction of CD/MD varies from 0 to 1, indicating the degree of fibre orientation in the paper, such that when fibres in the paper are randomly oriented, CD/MD equals 1; conversely, when fibres are unidirectionally oriented, the ratio is close to 0.

#### **4.2.2.3 Composite fabrication**

Aligned or randomly oriented short fibre mats were oven-dried at  $103^{\circ}\text{C}$  for 3 hours and then placed into a rectangular mould lined with a Teflon sheet. The epoxy resin and hardener were thoroughly mixed in a plastic cup and then degassed in a vacuum oven at room temperature for 10 minutes. The epoxy mixture was poured over the fibre and a wide flat ended metal scraper was used to spread resin over the mat and squeeze trapped air out. The resin impregnated fibre was degassed in its mould in a vacuum environment for 5 minutes to remove

trapped air and a Teflon sheet was placed on top and then the top part of the mould was positioned over the mould cavity. Finally, the mould was placed into a compression moulder and then the epoxy soaked fibre was pressed with pressures of 0.5, 2.0, 3.7, 7.0 and 9.0 MPa for fibre contents 12, 27, 33, 46 and 52 wt%, respectively, and left to cure for 24 hours. The composite sheet with nominal size of 22 x 15 x 0.3 cm was removed from the mould and post cured in an oven at 80°C for 4 hours.

#### **4.2.2.4 Tensile testing**

Composite tensile testing was based on ASTM D 3039 (Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials) using abrasive paper tabs within the grips. Five rectangular composite specimens with nominal dimensions of 150 x 15 x 3 mm were cut from cured composite sheets using a band saw. Specimen edges were then polished with an abrasive paper of grade 120. The tensile properties of neat epoxy were measured according to ASTM D 638 - 03 (Standard Test Method for Tensile Properties of Plastics). Six dumbbell-shaped epoxy specimens were cast and cured in a silicone mould for 24 hours and then post cured at 80°C in an oven for 4 hours. All tensile specimens were conditioned at  $23^{\circ} \pm 3^{\circ} \text{C}$  and  $50\% \pm 5\%$  relative humidity for at least 40 hours and then tested on an Instron-4204 universal testing machine fitted with a 50 kN load cell at a crosshead speed of 5 mm/min. Strain was measured using an Instron 2630-112 extensometer with a 50 mm gauge length. The mean value of tensile strength and Young's modulus of composites and neat epoxy were calculated.

#### ***4.2.2.5 Flexural testing***

Cured composites were cut into five flexural test specimens with nominal dimension of 70 x 12.7 x 3 mm using a band saw. The flexural test (three-point bending) was carried out in accordance with ASTM D 790-03 (Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials) on an Instron-4204 fitted with a 5 kN load cell. A support span of 48 mm and a crosshead speed of 2 mm/min were used. The average flexural strength and flexural modulus were calculated.

#### ***4.2.2.6 Density measurement***

The density measurement of composites was based on ASTM 792-00 (Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement). Distilled water was used as an immersion fluid. Densities of five cured epoxy and composite specimens were measured and the average density was obtained.

#### ***4.2.2.7 Microscopy***

An Olympus BX60F5 optical light microscope fitted with a Nikon camera (Digital Sight DS-U1) was used to study composite samples after flexural testing. Fibre surfaces and tensile fracture surfaces of composites were investigated using a Hitachi S4100 field emission scanning electron microscope (FESEM) operated at 5 kV. All samples were mounted on aluminium stubs using carbon tape and then sputter coated with platinum to make them conductive prior to observation.

## 4.3 Results and discussion

### 4.3.1 Fibre mat assessment

Figure 4.2 shows a fibre mat made using a DSF. It can be seen that fibres are distributed evenly in the mat and some degree of orientation could be observed. Fibre orientation was further assessed through tensile testing of mats in both longitudinal and transverse directions with results reported in Table 4.1 (values in parentheses are standard deviation). The ratio between transverse tensile strength (TTS) and longitudinal tensile strength (LTS) indicates the degree of fibre orientation. As previously mentioned, the lower the TTS/LTS ratio the higher the degree of fibre orientation. The ratio TTS/LTS for fibre mats produced using DSF can vary from 0.1 to 0.9. The ratio of 0.30 found in this work indicates good fibre alignment in the fibre mats.



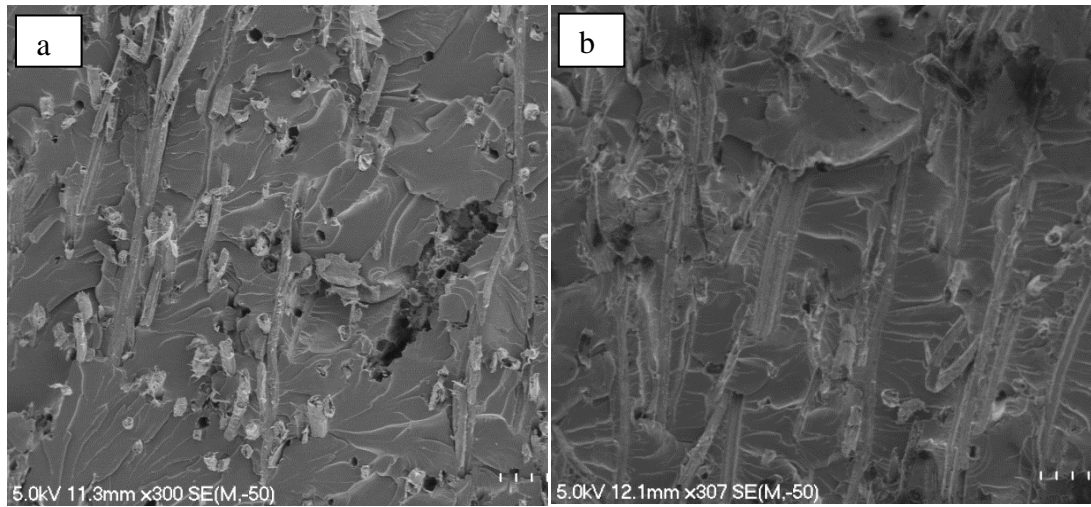
**Figure 4.2: Macrograph of an aligned fibre mat made from pulped harakeke fibre using DSF.**

**Table 4.1: Fibre mat tensile strengths.**

LTS (kN/m)	TTS (kN/m)	TTS/LTS
0.86 (0.04)	0.26 (0.01)	0.30

### 4.3.2 Evaluation of aligned short fibre composites

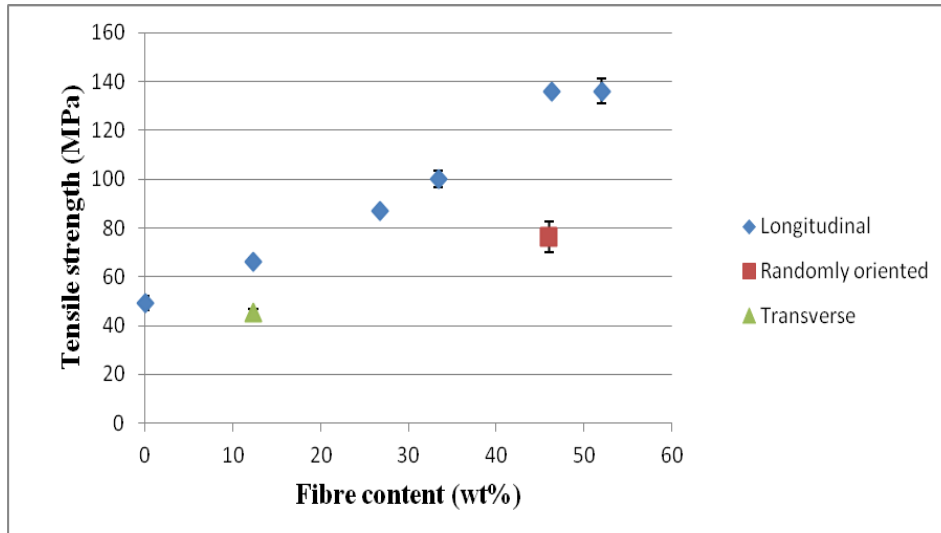
The alignment of fibres was also confirmed by SEM micrographs of tensile fracture surfaces of composites (Figure 4.3); more fibre ends appear on the images of longitudinal tensile tested sample while more fibre imprints present on transverse tensile one.



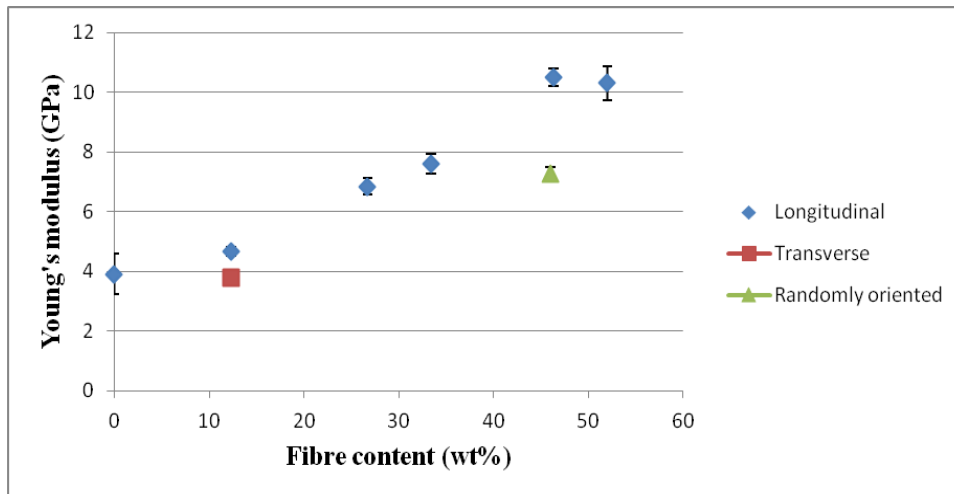
**Figure 4.3: SEM images of fracture surface of composites: (a) longitudinal tensile sample and (b) transverse tensile sample.**

Longitudinal tensile properties of composites with fibre contents of 12, 27, 32, 46 and 52 wt% are shown in Figures 4.4 and 4.5 along with transverse and randomly oriented fibre composites with fibre contents of 12 wt% and 46 wt%, respectively.





**Figure 4.4: Tensile strength of pulped harakeke fibre composite as a function of fibre content.**



**Figure 4.5: Young's modulus of pulped harakeke fibre composites as a function of fibre content.**

It can be seen that aligned harakeke fibre mats improved tensile strength and Young's modulus of the matrix even at a low fibre content of 12 wt% with increases of 35% and 19%, respectively. Both composite tensile strength and Young's modulus increased with fibre content up to 46 wt%. Further addition of fibres did not improve composite tensile strength or Young's modulus. The longitudinal tensile strength (LTS) of the composites containing 12 wt% fibre was 1.5 times higher than the transverse (TTS) giving a TTS/LTS ratio of 0.69

indicating that fibres were much more aligned on the longitudinal direction, a value higher than that for fibre mat due to the presence of a continuous phase (epoxy resin).

The tensile strength at 46 wt% fibre content of aligned short fibre composite (136 MPa) was 78.5% higher than that of randomly oriented fibre composite (76.2 MPa) and the increase of Young's moduli was 44.6 % (10.5 GPa compared to 7.26 GPa) supporting the improvement brought about by fibre orientation on tensile properties of short fibre composites. The maximum tensile strength and Young's modulus of 136 MPa and 10.5 GPa, respectively at fibre content of 46 wt% for longitudinal tensile tested samples are higher than any reported in the literature to date for natural fibre composites excluding those where hand-layup or a continuous fibre form has been produced and furthermore, these values overlap with those achieved using these procedures. So improved alignment here has more than compensated for the shorter length used, which also gives potential for use with waste fibre. Good bonding between pulped harakeke fibres and the matrix and fewer defects compared to bast fibres which were discussed in Chapter 3 are likely to have contributed to the tensile properties of pulped harakeke fibre-epoxy composites. However, the main reason appears to be due to fibre alignment as discussed above.

#### **4.3.3 Evaluation of flexural properties of aligned short fibre composites**

During flexural loading, composite samples did not break completely with specimens still remaining intact. Cracks appeared on the tension surface of the sample and propagated to the middle through the sample thickness and debonding

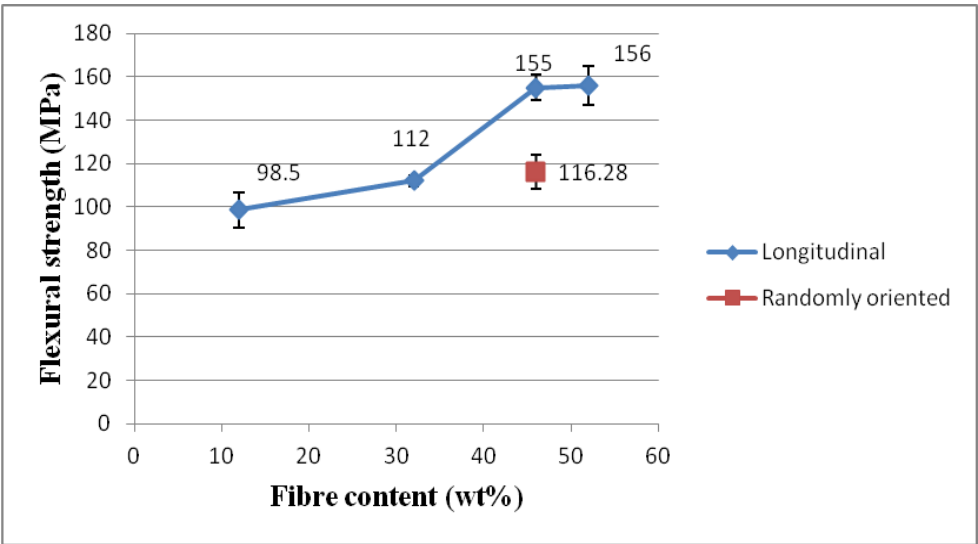
occurred supporting that bending failure was not only governed by tension but also shear (Figure 4.6).



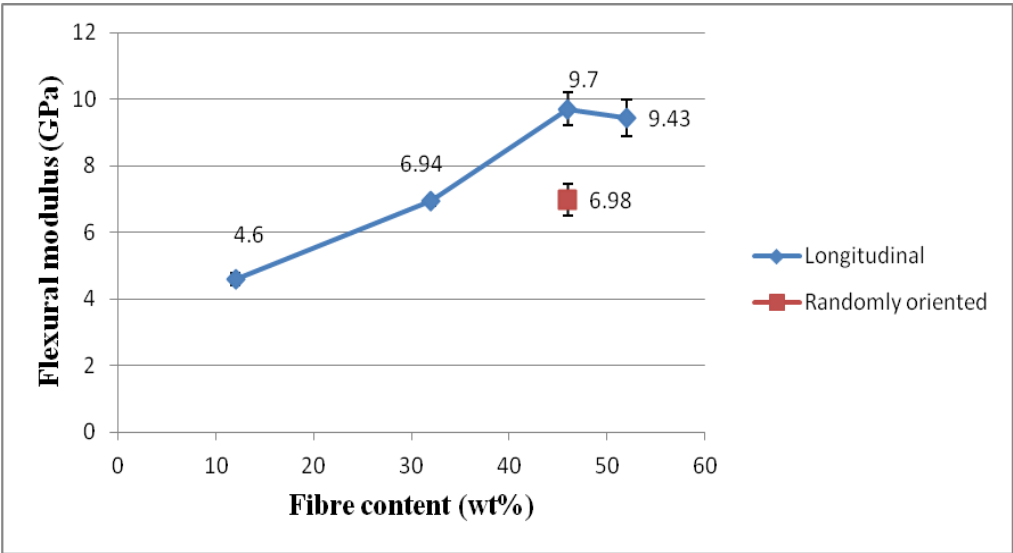
**Figure 4.6: Micrograph captured from the side of flexural testing sample (the scale bar denotes 20 micron).**

The flexural properties of aligned short composites are presented in Figure 4.7 and 4.8. It can be seen that both flexural strength and modulus increased with fibre content up to 46 wt%. As for tensile properties, with higher fibre content, the flexural properties did not improve. The maximum values for flexural strength and modulus were 155 MPa and 9.7 GPa, respectively at the fibre content of 46wt%. This strength is lower but the modulus higher than for pulped harakeke fibre reinforced epoxy composites previously reported in the literature [33] where long fibre bundles were pulped such that the full length of single fibre was maintained (3.5-5.5 mm) and hand placement was used, while the shorter fibre length (1.97 mm) used in our study would explain composites with lower flexural strength obtained here, albeit with the potential to be automatically produced by

DSF. The flexural strength and modulus of aligned short fibre composites containing 46 wt% fibres were 34% and 39% higher than those of randomly oriented fibre, respectively. These figures are significantly lower than those for improvement of tensile properties.



**Figure 4.7: Flexural strength of pulped harakeke fibre composites as a function of fibre content.**



**Figure 4.8: Flexural modulus of pulped harakeke fibre composites as a function of fibre content.**

#### 4.3.4 Determining fibre orientation factors

Given that fibre orientation is influential on performance, it is valuable to be able to assess the degree of orientation. Confusion arises in the literature regarding the use of orientation factors. Although different values are found from composite strength and stiffness with their respective modified Rule of Mixtures equations [123; 124], orientation factors used to predict strength and stiffness are sometimes assumed to be the same [125]. In this work, orientation factors are evaluated for strength and stiffness separately.

##### 4.3.4.1 Fibre orientation factor for Young's modulus.

Young's modulus of aligned short harakeke fibre - epoxy composites taking account of composite porosity can be estimated using the modified Rule of Mixtures:

$$E_c = \eta_o \eta_l E_f V_f + V_m E_m \quad (4.2)$$

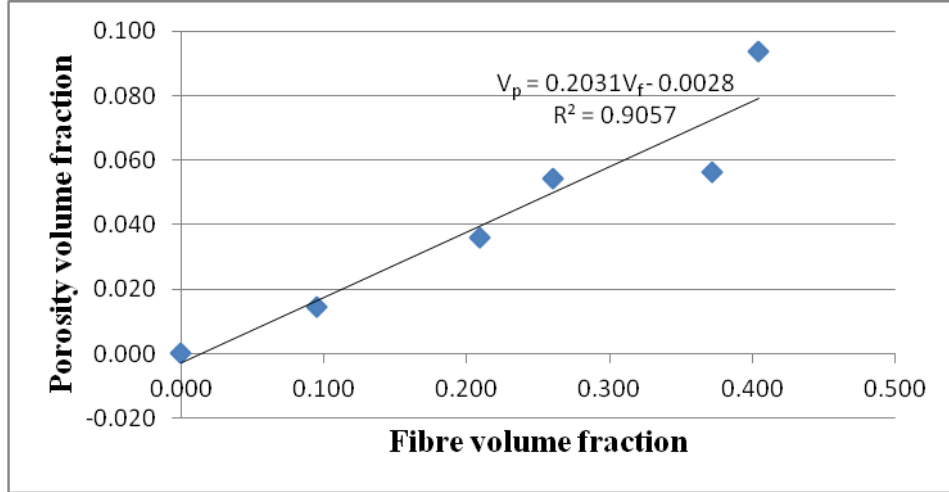
with

$$V_m = 1 - V_f - V_p \quad (4.3)$$

$$V_f = W_f(\rho_c/\rho_f) \quad (4.4)$$

where  $\rho$ ,  $E$ ,  $W$  and  $V$  are density, Young's modulus, weight fraction and volume fraction, respectively; subscripts c, f, m and p denote composite, fibre, matrix and porosity, respectively;  $\eta_o$  and  $\eta_l$  are orientation efficiency factor and length efficiency factor, respectively. Values from the literature include  $\eta_o = 1$  for unidirectional composites,  $\eta_o = 0.5$  for bidirectional, balanced (0/90°),  $\eta_o = 0.375$  for 2D random and  $\eta_o = 0.2$  for 3D random [126; 127].

Porosity of composites has been found to be a function of fibre content [128; 129]. In this work, the porosity was modelled as a linear function of fibre volume fraction using linear regression modelling as shown in Figure 4.9



**Figure 4.9: Porosity as a function of fibre volume fraction.**

$$V_p = 0.2031V_f - 0.0028 \quad (4.5)$$

Substituting  $V_p$  from Equation 4.5 into Equation 4.2, leads to:

$$E_c = \eta_o \eta_l E_f V_f + (1.0028 - 1.2031V_f)E_m \quad (4.6)$$

or

$$E_c = (\eta_o \eta_l E_f - 1.2031E_m)V_f + 1.0028E_m \quad (4.7)$$

The fibre length efficiency factor ( $\eta_l$ ) can be calculated using the shear lag model originally developed by Cox [130]:

$$\eta_l = 1 - \tanh(\beta L/2) / (\beta L/2) \quad (4.8)$$

$$\text{where } \beta L/2 = (2L/d) \sqrt{G_m/E_f \ln\left(\frac{k}{V_f}\right)} \quad (4.9)$$

where  $L$  is fibre length,  $d$  is fibre diameter,  $G_m$  is shear modulus of matrix,  $V_f$  is fibre volume fraction,  $k$  is a constant dependant on geometrical packing pattern of fibres [131], equal to 0.907 and 0.785 for hexagonal and square packing respectively.

Assuming  $k = 0.785$ ,  $G_m = E_m/2(1+\nu) = 1.117$  GPa with Poisson's ratio of epoxy  $\nu = 0.35$  [132], Young's modulus of the matrix,  $E_m = 3.91$  GPa (Figure 4.5),  $L = 1.97$  mm and  $D = 15.67$   $\mu\text{m}$  (Table 3.1), the fibre length factors  $\eta_l$  for different fibre contents were calculated and shown in Table 4.2.

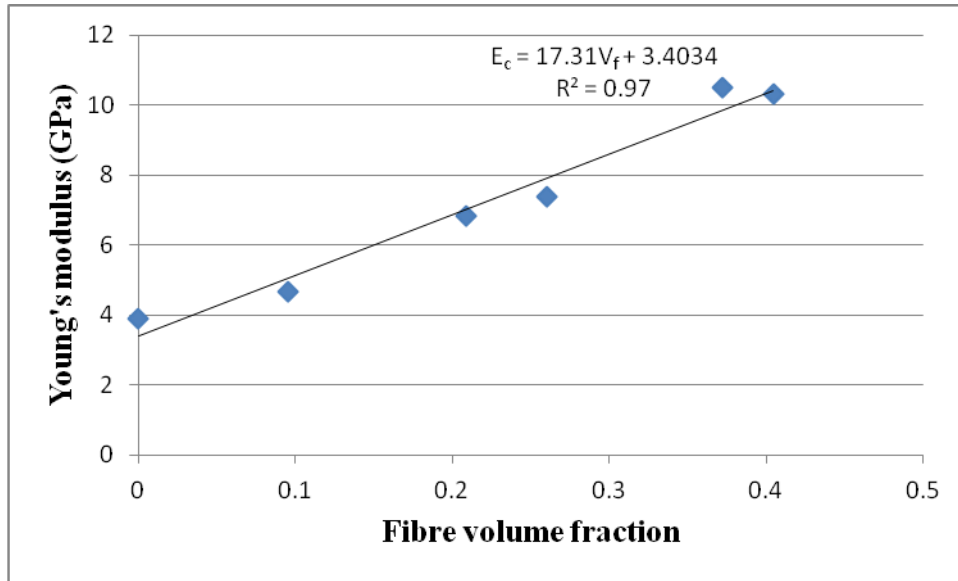
**Table 4.2: Physical properties of pulped harakeke fibre composites.**

Wt%	$W_f$	$\rho_c$ (g/cm <sup>3</sup> )	$V_f$	$\rho_{ct}$ (g/cm <sup>3</sup> )	$V_p$	$\eta_l$
12.3	0.123	1.175	0.095	1.192	0.015	0.9892
26.7	0.267	1.189	0.209	1.234	0.036	0.9914
33.4	0.334	1.184	0.260	1.252	0.054	0.9922
46.3	0.463	1.22	0.372	1.293	0.056	0.9936
52	0.520	1.182	0.404	1.304	0.094	0.9939

Using linear regression parameters shown in Figure 4.10 and comparing with Equation 4.7, it can be seen that

$$\eta_o \eta_l E_f - 1.2031 E_m = 17.31 \quad (4.10)$$

Substituting  $E_f = 47.6$  GPa (Table 3.1),  $E_m = 3.91$  GPa [129] and  $\eta_l = 0.99$  (Table 4.2) into Equation 4.10 gives  $\eta_o = 0.467$  which corresponds to an average orientation angle  $\alpha = 34^\circ$  considering  $\eta_o = \cos^4(\alpha)$  [124; 126].



**Figure 4.10: Young's modulus as a function of fibre volume fraction including regression equation and R-square value.**

#### **4.3.4.2 Fibre orientation factor for tensile strength calculation.**

The orientation factor for tensile strength can be estimated using the Bowyer-Bader method [133] that was developed from the Kelly-Tyson model [134]. In the Bowyer-Bader model, it can be assumed that at any composite stress there is a critical fibre length ( $L_c$ ) such that at the centre of the fibre, the strain of the matrix and fibre are the same and the spectrum of fibre lengths in the composite can be considered to be divided into subcritical subfractions (denoted  $L_i$ ) and supercritical subfractions (denoted  $L_j$ ) and their volume fractions are  $V_i$  and  $V_j$ , respectively. The tensile stress on a composite can be estimated according to Equation 4.11.

$$\sigma_c = k_1 X + k_1 Y + Z \quad (4.11)$$



where X, Y and Z are the contributions of subcritical fibres, supercritical fibre and matrix respectively;  $k_1$  is a fibre orientation factor. They are expanded in following equations:

$$X = \sum \frac{\tau L_i V_i}{d} \text{ with } L_i < L_e \quad (4.12)$$

$$Y = \sum E_f \varepsilon_c (1 - E_f \varepsilon_c d / 4 L_j \tau) V_j \text{ with } L_j > L_e \quad (4.13)$$

$$Z = \sigma_m V_m \quad (4.14)$$

where  $\tau$  is interfacial shear strength between fibre and matrix;  $d$  is fibre diameter;  $V_m$  was calculated as in Equation 4.3, and

$$L_e = (E_f \varepsilon_c d) / (2\tau) \quad (4.15)$$

Values of composite strains at two levels  $\varepsilon_1$  and  $\varepsilon_2$  are chosen so that  $\varepsilon_2 = 2\varepsilon_1$ . The composite stresses  $\sigma_{c1}$  and  $\sigma_{c2}$  and matrix stresses  $\sigma_{m1}$  and  $\sigma_{m2}$  corresponding to  $\varepsilon_1$  and  $\varepsilon_2$  are determined from stress-strain curves of composites and matrix, respectively. With these data, the ratio R can be determined.

$$R = (\sigma_{c1} - Z_1) / (\sigma_{c2} - Z_2) \quad (4.16)$$

To calculate  $k_1$  a value of  $\tau$  need to be assumed and the corresponding  $L_{e1}$  and  $L_{e2}$  calculated using Equation 4.15. Values of X and Y can then be determined using assumed values of  $L_{e1}$ ,  $L_{e2}$  and  $\tau$  and fibre length distribution. With these assumed values, the ratio R' can be calculated, such that

$$R' = (X_1 + Y_1) / (X_2 + Y_2) \quad (4.17)$$

The value of  $\tau$  can then be adjusted until  $R = R'$ . This figure can be assumed to be correct and  $k_1$  determined by applying this value to Equation 4.11.

The experimental data and fibre length distribution used in the Bowyer-Bader model are presented in Table 4.3 and Figure 4.11, respectively.

**Table 4.3: Input data for Bowyer-Bader model.**

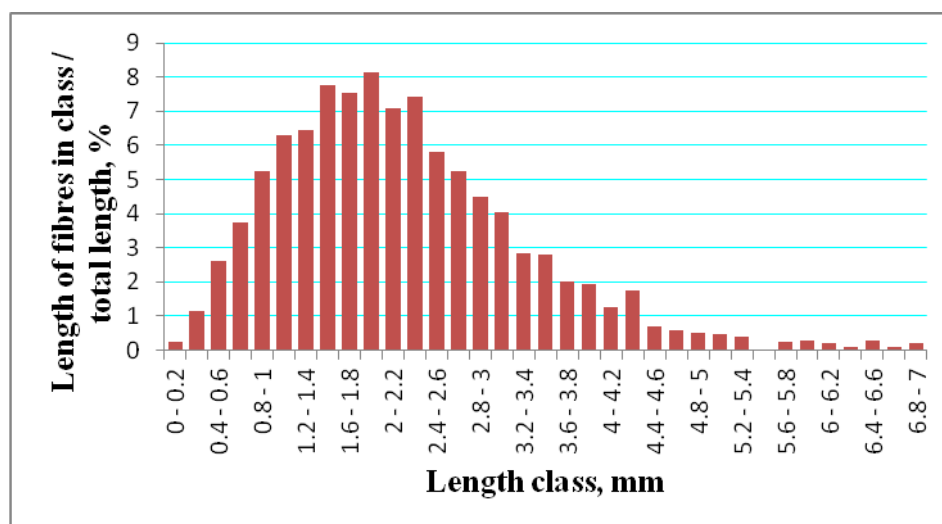
Fibre content wt%	12	27	33	46	52	48 RO
$V_f$	0.095	0.209	0.260	0.372	0.404	0.389
$\epsilon_1(\%)$	0.70	0.79	0.80	0.79	0.84	0.71
$\epsilon_2(\%)$	1.40	1.57	1.61	1.57	1.68	1.42
$\epsilon_{\max}(\%)$	2.10	2.36	2.41	2.36	2.52	2.13
$\sigma_{c1}(\text{MPa})$	29.3	42.8	45.6	68.0	65.3	64.0
$\sigma_{c2}(\text{MPa})$	49.6	69.6	73.7	109.0	103.0	101.0
$\sigma_{\text{cmax}}(\text{MPa})$	66.20	87.2	100	136	137	76.2
$\sigma_{m2}(\text{MPa})$	19.90	21.5	21.5	21.5	21.5	19.2
$\sigma_{m2}(\text{MPa})$	36.50	38.8	38.8	38.8	38.8	35.5
$\sigma_{\text{mmax}}(\text{MPa})$	46.5	47.7	48.0	47.7	48	45.8
$E_f(\text{GPa})$	47.60	47.60	47.60	47.60	47.60	47.60
$d(\mu\text{m})$	15.67	15.67	15.67	15.67	15.67	15.67

Orientation factors and IFSS values are reported in Table 4.4. It can be seen that values of fibre orientation factors for aligned fibre composites at different fibre contents were similar indicating constant orientation despite higher pressure being applied at higher fibre contents. The mean value of orientation factor of 0.505 obtained for aligned fibre composites is significantly higher than that obtained for injection moulded natural fibre composites using the same method of determination [124; 135]. It is also much higher than that for randomly oriented fibre composite (0.312) found in this work which supports that DSF can produce

fibre mats with good fibre alignment. The value of orientation factor for tensile strength (0.505) is higher than that for Young's modulus (0.467). However, when comparing their fibre orientation angles, the difference was very small; 33° for tensile strength and 34° for Young's modulus, although it is possible that orientation at fracture where strength is assessed is slightly higher than at lower strain where Young's modulus is assessed.

**Table 4.4: Fibre orientation factors and interfacial shear strengths.**

Fibre content wt%	12	26	33	46	52	46 RO
Orientation factor $k_1$	0.505	0.483	0.489	0.531	0.517	0.312
Orientation angle (°)	33	34	33	31	32	42
IFSS (MPa)	2.61	3.14	3.17	3.37	3.23	2.47



**Figure 4.11: Harakeke fibre length distribution.**

#### **4.4 Chapter conclusion**

Dynamic sheet forming has been shown to be a potential technique to produce aligned short natural fibre mats for composite production using compression moulding. Aligned short harakeke fibre-epoxy composites were produced with this technique with high tensile strength and Young's modulus of 136 MPa and 10.5 GPa, respectively. Fibre orientation factors were also estimated with values of 0.505 and 0.467 relating to average fibre orientation angles of  $34^{\circ}$  and  $33^{\circ}$  from values of composite tensile strength and Young's modulus, respectively.

## **Chapter Five: Aligned long harakeke/epoxy composites**

### **5.1 Introduction**

In this work, aligned long harakeke fibre reinforced epoxy composites were prepared using compression moulding. The tensile and flexural properties of the composites with various fibre volume fractions were evaluated and a model was developed for predicting tensile strength of aligned long harakeke-epoxy composites.

### **5.2 Experimental**

#### **5.2.1 Materials**

Harakeke fibre bundles as supplied from the Templeton Flax Mill, Riverton, New Zealand were combed manually in a single direction before being cut to the same length as that of compression mould, and then dried at 80°C overnight before composite fabrication. The matrix was a low viscosity epoxy system comprising of Nuplex resin R180 and Nuplex standard hardener H180 (mixing ratio 5:1 by weight).

#### **5.2.2 Methods**

##### ***5.2.2.1 Composite manufacture***

The fabrication of harakeke/epoxy composites was similar to that which has been used to make flax/epoxy composites [74]. Combed and dried continuous fibre bundles were hand laid into a simple rectangular mould (size: 22 x 15 x 0.3 cm), which had been lined by a Teflon sheet, to form a fibre mat. Composites with six different nominal fibre contents (15, 25, 35, 45, 55 and 65 wt%) were produced.

The epoxy resin and hardener were thoroughly mixed in a plastic cup and then degassed in a vacuum oven at room temperature for 10 minutes. The epoxy mixture was poured over the fibre mat and a wide flat ended metal scraper was used to spread resin over the mat and squeeze trapped air out. The resin impregnated fibre mat was left for resin to soak into the mat for 20 minutes before being degassed in a vacuum environment for 5 minutes to remove trapped air. A steel plate was then laid on the top of the mould. Finally, the mould was placed into a compression moulder and then the epoxy soaked fibre mat was pressed until the mould closed and was left for curing for 24 hours. Due to resin coming out from the mould during pressing, fibre content was calculated based on weight of fibre and composites. The composite sheet was removed from the mould and post cured for 4 hours in an oven at 80°C.

#### ***5.2.2.2 Composite density, fibre volume and porosity measurement***

The density measurement of composites was based on ASTM 792-00 (Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement). Distilled water was used as an immersion fluid. Densities of five cured epoxy and composite specimens were measured and the average density was obtained.

Fibre and matrix volume fraction were calculated using the equations [1]:

$$V_f = W_f(\rho_c/\rho_f) \quad (5.1)$$

$$V_m = 1 - V_f - V_p \quad (5.2)$$

where  $V$ ,  $W$  and  $\rho$  are volume fraction, weight fraction and density, respectively; subscripts  $f$ ,  $m$ ,  $p$  and  $c$  denotes fibre, matrix, porosity and composite, respectively.

Total porosity of composites was calculated using the equation [136]:

$$V_p = (\rho_{ct} - \rho_c) / \rho_{ct} \quad (5.3)$$

where:

$$\rho_{ct} = \rho_f V_f + \rho_m V_m \quad (5.4)$$

such as  $\rho_{ct}$  is theoretical density of composites.

Composite porosity due to the fibre lumen is:

$$P_l = V'_l V_f \quad (5.5)$$

where  $V'_l$  is lumen volume fraction in fibre bundles determined in Chapter 3

### **5.2.2.3 Composite tensile testing**

Composite tensile testing was based on ASTM D 3039 (Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials) using abrasive paper tabs within the grips. Six composite specimens with nominal dimensions of 200 x 15 x 3 mm were cut from cured composite sheets using a circular saw. The longest specimen edges were then polished using abrasive paper. The tensile properties of neat epoxy were measured according to ASTM D 638 - 03 (Standard Test Method for Tensile Properties of Plastics). Six dumbbell-shaped epoxy specimens were cast and cured in a silicone mould for 24 hours and then post cured at 80°C in an oven for 4 hours. All tensile specimens were conditioned at

23° ± 3° C and 50% ± 5% relative humidity for 40 hours and then tested on an Instron-4204 universal testing machine fitted with a 50 kN load cell at a crosshead speed of 5 mm/min. Strain was measured using an Instron 2630-112 extensometer with a 50 mm gauge length. The mean value of tensile strength and Young's modulus of composites and neat epoxy were calculated.

#### ***5.2.2.4 Composite flexural testing***

Cured composites were cut into six flexural test specimens with nominal dimension of 85 x 12.7 x 3 mm using a circular saw. The longest specimen edges were then polished with abrasive paper. The flexural test (three-point bending) was carried out in accordance with ASTM D 790-03 (Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials) on an Instron-4204 fitted with a 5 kN load cell. A support span-to-depth ratio of 16:1 and a crosshead speed of 2 mm/min were used. The average flexural strength and flexural modulus were calculated.

#### ***5.2.2.5 Composite impact testing***

The impact testing was carried out according to the EN ISO 179 Plastics – Determination of Charpy impact strength using a Ray-Ran Pendulum Charpy Impact System machine. The impact velocity of 3.5 m/s and the hammer weight of 1.188 kg were used. Dimensions of the samples were 80 x 8 x 3.5 mm<sup>3</sup> with a single notch of 0.25 mm. Five specimens were tested for each batch of samples.



#### **5.2.2.6 Fracture toughness ( $K_{IC}$ ) testing**

Mode I fracture toughness ( $K_{IC}$ ) of single-edge-notched-bend (SENB) specimens were measured according to the ASTM D 5045-99 Standard Test Methods for Plane-Strain Fracture Toughness and Strain Energy Release Rate of Plastic using an Instron-4204 universal testing machine fitted with a 5 kN Load cell with a crosshead speed of 10 mm/s. Five specimens for each batch of composites were tested.

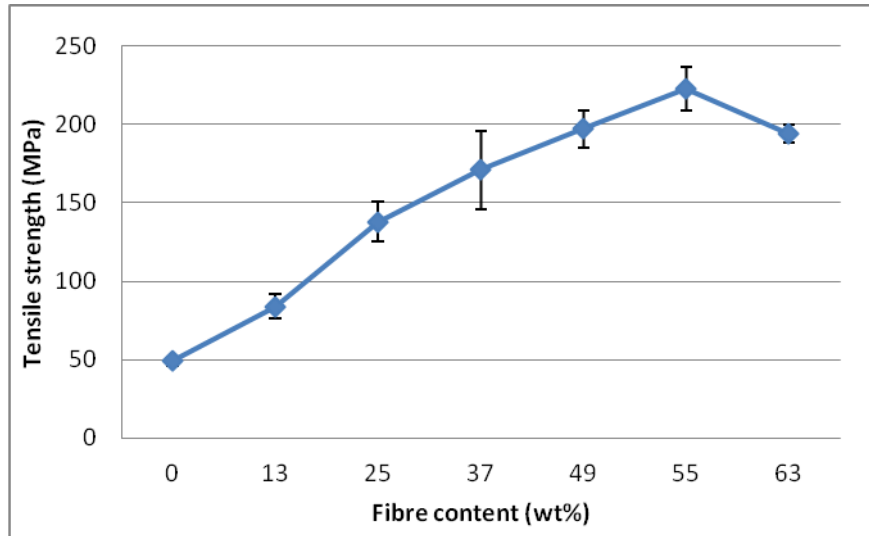
#### **5.2.2.7 Microscopy**

A WILD M3B stereo microscope fitted with a Nikon camera (Digital Sight DS-U1) was used to study composite sample surfaces after flexural testing. Tensile fracture surfaces of composites were investigated using a Hitachi S4100 field emission scanning electron microscope (FESEM) operated at 5 kV. All samples were mounted on aluminium stubs using carbon tape and then sputter coated with platinum to make them conductive prior to observation.

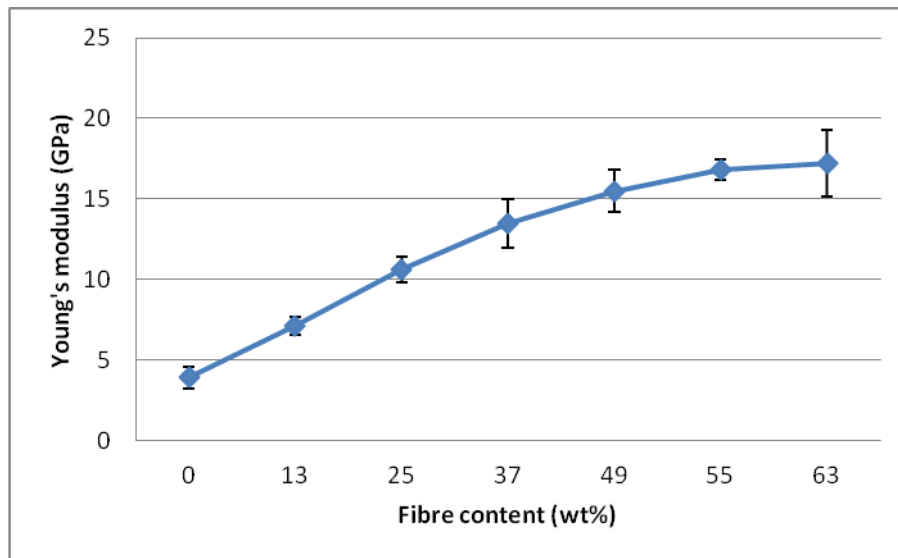
### **5.3 Results and discussion**

#### **5.3.1 Composite tensile properties**

Average tensile strength and Young's modulus of composite specimens with different fibre weight fractions and cured epoxy specimens are presented in Figures 5.1 and 5.2, respectively.



**Figure 5.1: Tensile strength of harekeke/epoxy composites versus fibre volume fraction; each error bar corresponds to one deviation.**



**Figure 5.2: Young's modulus of harekeke/epoxy composites versus fibre volume fraction; each error bar corresponds to one deviation.**

These figures show that the addition of harakeke fibre makes epoxy stronger and stiffer even at a fibre content as low as 13wt% which provided an increase of 71% and 82% for the tensile strength and Young's modulus, respectively. Tensile strength and Young's modulus can be seen to share the same trend of increase

with fibre volume fraction up to a fibre content of 55wt%. At a fibre content of 55wt%, the average tensile strength and Young's modulus of harakeke fibre composites were 223 MPa and 16.8 GPa, which are 4.6 fold and 4.3 fold higher than those of neat epoxy, respectively. These figures compare well with the results of 211 MPa and 14.7 GPa for tensile strength and Young's modulus, respectively, reported in the literature on harakeke-epoxy composites at the same fibre volume fraction [57]. However, as fibre content increased to 63wt%, tensile strength of harakeke fibre decreased to 193 MPa, although Young's modulus increased modestly to 17.2 GPa. This can be explained in that at this high fibre content, the wetting of fibre by epoxy became worse resulting in weaker fibre/matrix bonding which caused the reduction of composite tensile strength. However, with fibre bonding not being so important to Young's modulus, this still increased further with higher fibre content.

Table 5.1 shows the absolute and specific tensile properties of harakeke based composites compared to glass and other cellulose based fibre reinforced epoxy composites with the same fibre configuration (aligned long fibre).

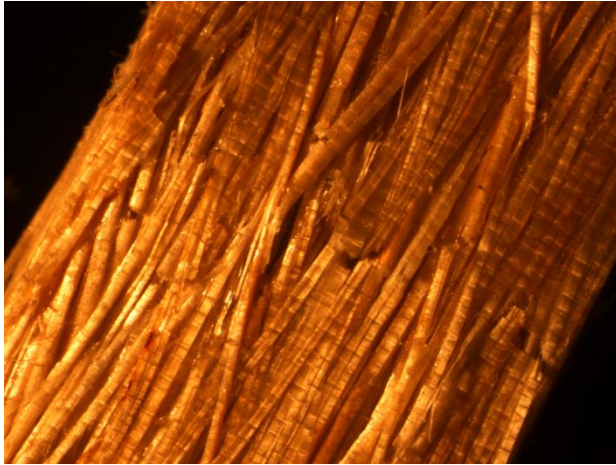
It can be seen that tensile strength and Young's modulus of harakeke fibre composites are lower than those of glass fibre composite but the difference between specific Young's moduli is small; 15.6 GPa.g/cm<sup>3</sup> for harakeke fibre composites compared to 18 GPa.g/cm<sup>3</sup> for glass fibre composites. The tensile strength of the harakeke fibre composites ( $223 \pm 14$  MPa) is greater than that of the sisal fibre composites ( $211 \pm 12$  MPa) but the Young's modulus of the sisal fibre composites is higher ( $19.7 \pm 1.5$  GPa, compared to  $16.8 \pm 0.62$  GPa).

**Table 5.1: Comparison of harakeke composite tensile properties with glass and other natural fibre composites (standard deviation values in parenthesis).**

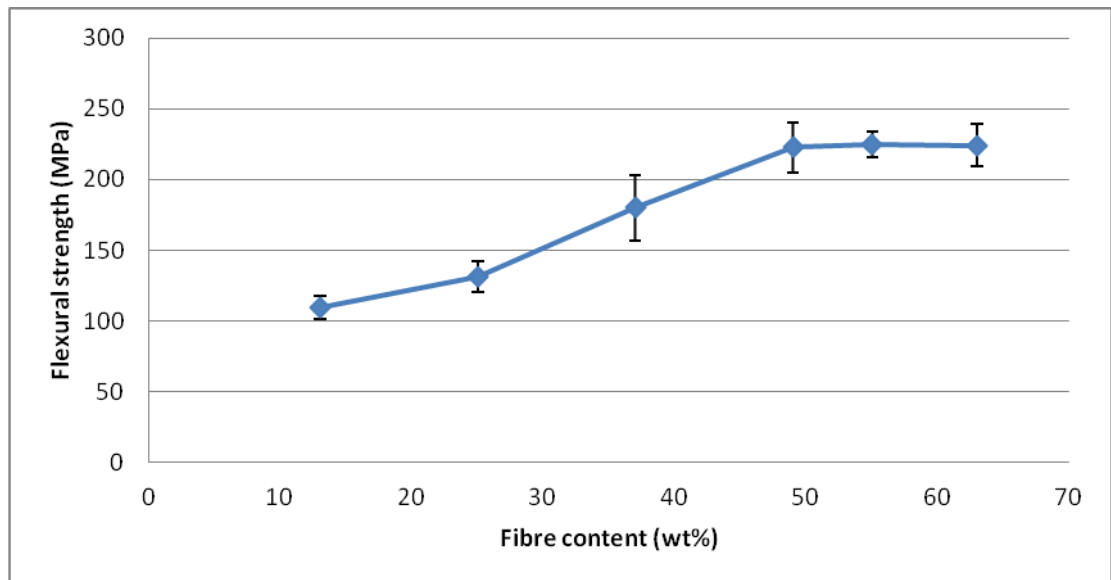
Fibre	Fibre content (%)	Density (g/cm <sup>3</sup> )	Tensile strength (MPa)	Specific strength (MPa.g /cm <sup>3</sup> )	Young's modulus (GPa)	Specific Young's modulus (GPa.g /cm <sup>3</sup> )	Failure strain (%)	Ref
	0	1.16	49.2		3.91		2.91	-
Harakeke	55	1.04	223 (14)	214	16.8 (0.62)	16.2	1.44	-
Harakeke	50	1.16	211 (10)	181	14.7 (0.8)	12.6		[57]
Sisal	46		211 (12)	180	19.7 (1.5)	16.8		[137]
Hemp	65		165	-	17	-		[83]
Flax	40		133		28			[138]
Glass	48		817	487	31	18		[139]

### 5.3.2 Composite flexural properties

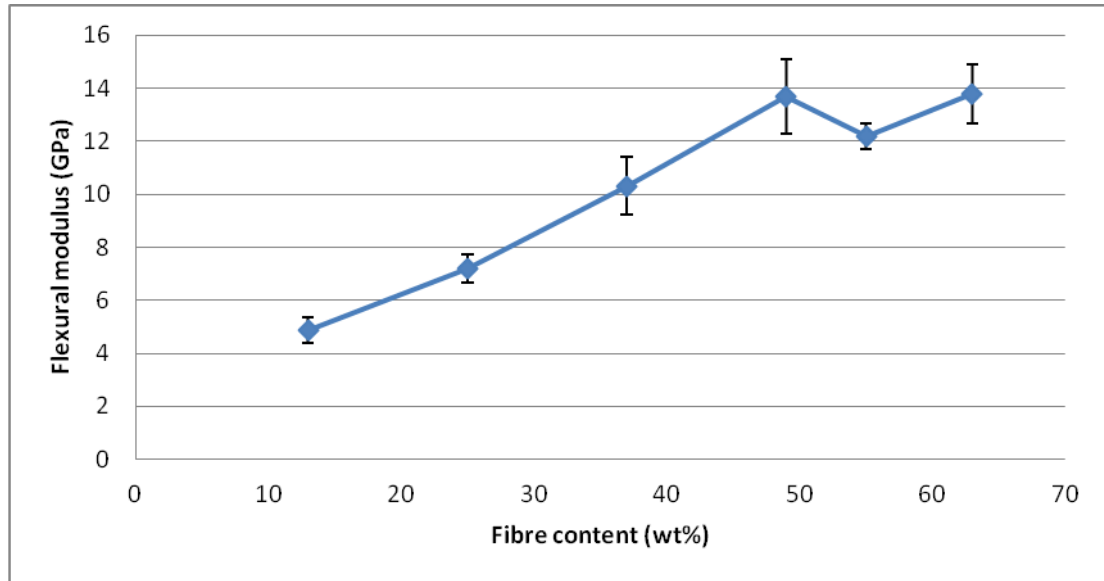
Micrographs of composites after flexural testing are shown in Figure 5.3. It appears that composite samples did not fail after the test but micro crack happened on the tension surface. Average flexural strength and flexural modulus of aligned long harakeke reinforced epoxy composites with different fibre contents are presented in Figures 5.4 and 5.5, respectively, for the first time.



**Figure 5.3: Tension surface stereomicroscope micrograph of composites after flexural testing**



**Figure 5.4: Flexural strength of harakeke/epoxy composites versus fibre volume fraction; each error bar corresponds to one deviation.**



**Figure 5.5: Flexural modulus of harakeke/epoxy composites versus fibre volume fractions; each error bar corresponds to one deviation.**

It can be seen that the flexural strength and flexural modulus of harakeke/epoxy composites increases as the fibre content increased up to 49wt%. The trend is similar to that for pulped harakeke fibre reinforced epoxy reported in the literature [33] with fibre content up to 50wt%. However, in this research, flexural properties at higher fibre contents were not investigated so their trend above 50wt% was not reported. The maximum flexural strength and modulus of about 190 MPa and 9.5 GPa, respectively, were found at a fibre content of about 50wt%, which are lower than the figures found in our work with 223 MPa and 13.7 GPa for tensile strength and Young's modulus respectively. Further addition of harakeke fibre above a fibre content of 49% did not bring about improvement of these flexural properties. As can be seen in Figure 4.6, debonding occurred during flexural testing. At high fibre contents, wetting between harakeke fibres and epoxy matrix was poorer which could result in a more severe debonding and therefore flexural properties were not improved at fibre contents higher than 49%.

### 5.3.3 Modelling of tensile properties of long aligned harakeke fibre composites

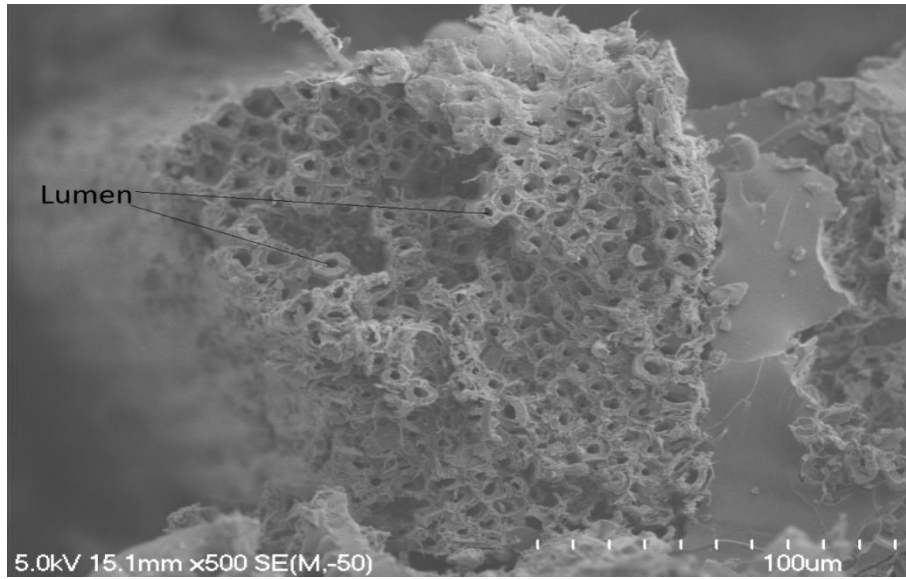
#### 5.3.3.1 Fibre volume fraction and porosity

Values of fibre volume fraction, matrix volume fraction, total porosity and lumen porosity are presented in Table 5.2.

**Table 5.2: Physical properties of harakeke composites.**

Fibre weight fraction	Composite density (g/cm <sup>3</sup> )	Fibre volume fraction	Total porosity volume fraction	Lumen porosity volume fraction
0.131	1.143 (0.004)	0.118	0.025 (0.003)	0.025
0.248	1.112 (0.017)	0.216	0.060 (0.014)	0.046
0.369	1.086 (0.013)	0.315	0.091 (0.011)	0.067
0.490	1.041 (0.027)	0.400	0.135 (0.022)	0.086
0.549	1.041 (0.031)	0.449	0.139 (0.024)	0.096
0.630	1.010 (0.021)	0.499	0.169 (0.018)	0.107

Significant porosity is typical for natural fibre composites, but has largely been ignored in modelling. However Madsen et al have taken account of porosity relating to processing (matrix porosity and that at the fibre/matrix interface) although due to fibre collapse in their work, lumens were not considered to contribute to this [127; 128]. However, for the harakeke composites investigated in the present work, fibre lumens did not collapse (see Figure 5.6) and contributed significantly to composite porosity (Table 5.2) due to the large lumen fraction in fibre bundles as mentioned in Chapter 3.

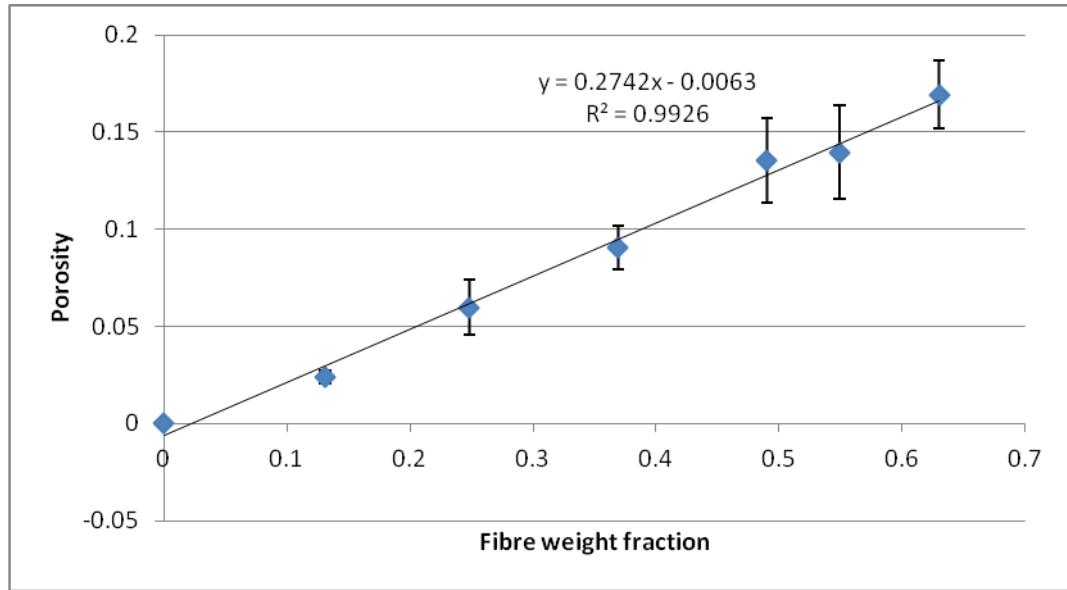


**Figure 5.6: FESEM harakeke fibre bundles in composites showing clear lumens**

It is appreciated that the values of lumen porosity were obtained based on the assumption that the density of single fibres was the same as that of the fibre bundles, however, given the value of  $1.27 \text{ g/cm}^3$  for fibre bundle density and the maximum possible value for single fibres being that for pure crystallised cellulose of  $1.5 \text{ g/cm}^3$  [140], this reflects a maximum possible overestimate of 15% for lumen porosity and therefore, lumen porosity can still be considered to be the major component of porosity. However, this assumption did not affect the total porosity which was calculated from theoretical and actual composite densities and total porosity would be used in modelling discussed later. The total porosity was assumed to be a variable function of the fibre weight fraction [128]. For simplicity, the total porosity fraction was assumed to be a linear function as presented in Figure 5.7 using data in Table 5.2 and found to be well approximated by:

$$V_p = 0.2742W_f - 0.0063 \quad (5.5)$$





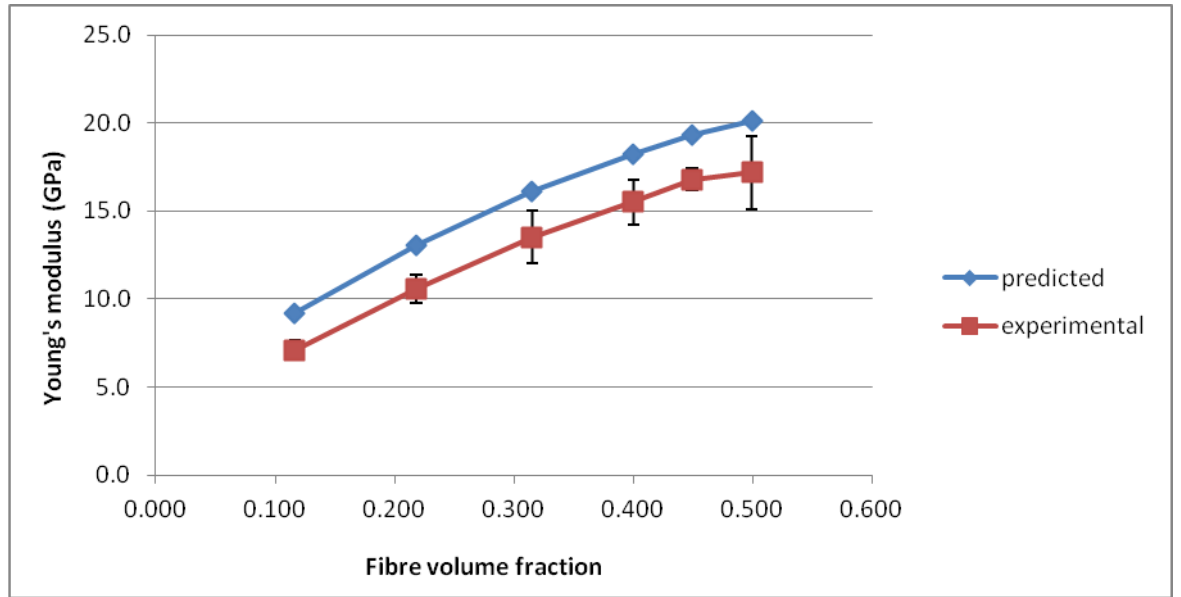
**Figure 5.7: Porosity modelling with linear equation; each error bar corresponds to one standard deviation.**

### 5.3.3.2 Young's modulus

Young's modulus of aligned long harakeke composites ( $E_c$ ) may be predicted using the Rule of Mixtures considering the effect of composite porosity [127; 128]:

$$E_c = (E_f V_f + E_m V_m)(1 - V_p)^2 \quad (5.6)$$

where  $E$  is Young's modulus and  $V_p$  was substituted from Equation 5.5 . Results of Young's modulus predictions are presented in Figure 5.8. The predicted Young's moduli are 13 - 29% higher than experimental ones depending on fibre volume fractions.



**Figure 5.8: Predicted Young's modulus (PYM) and experimental Young's modulus (EYM) of harakeke/epoxy composites as a function of fibre volume fraction; each error bar corresponds to one deviation.**

### 5.3.3.3 Tensile strength

The composite strength ( $\sigma_c$ ) may be estimated using the Rule of Mixtures including porosity as follows [128]:

$$\sigma_c = (\sigma_f V_f + \sigma_m V_m)(1 - V_p)^2 \quad (5.7)$$

where  $\sigma_f$  and  $\sigma_m$  are fibre strength and matrix strength, respectively. This equation assumes a perfect interface which, given epoxy as a matrix, would appear to be a reasonable assumption. Corrected average tensile strength of the fibre and tested average tensile strength of the matrix were substituted into Equation 5.7 and the predicted and experimental strengths assuming a perfect interface for the composites are shown in Table 5.3. The predicted values were found to be larger than the experimental ones by 135% to 243% depending on fibre volume fraction.

**Table 5.3: Comparison of predicted and experimental tensile strength of harakeke composites using average fibre and matrix tensile strength.**

Fibre volume fraction	Predicted strength (MPa)	Experimental strength (MPa)	Prediction error (%)
0.117	197	84	135
0.218	326	138	136
0.315	449	171	163
0.400	557	197	183
0.449	619	223	178
0.499	683	199	243

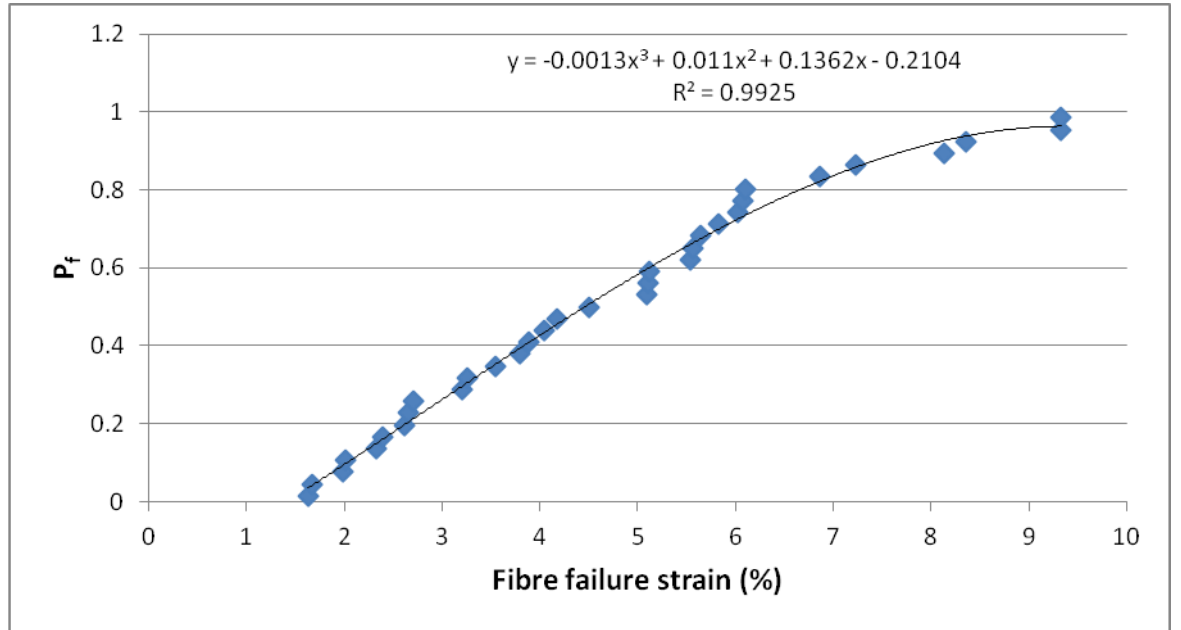
Due to the large gap between predicted and experimental tensile strengths of the composites, an alternative model for predicting the tensile strength of the aligned long fibre composites was considered. It can be seen that the average fibre and epoxy matrix failure strains as reported in Chapter 3 are 4.54% and 2.91% , respectively, which at first sight does not explain composites failing at a lower average strain of about 1.44%. However, due to the variability of natural fibre properties, some fibres would have failed at strains lower than their average failure strain; fibre failure strain varied significantly with standard deviation of 2.35% equivalent to a coefficient of variation of 36.3%. Therefore, it was assumed that composite failure could be initiated when fibres with the lowest failure strain failed giving a lowest fibre failure strain based Rule of Mixtures model expressed by:

$$\sigma_c = (\sigma_f^* V_f + \sigma_m^* V_m) \cdot (1 - V_p)^2 \quad (5.8)$$

where now  $\sigma_f^*$  and  $\sigma_m^*$  are the fibre stress and matrix stress at the failure strain of the weakest fibres. These values were taken as the average stresses of all the tested fibres and epoxy samples, respectively, at the lowest failure strain of all the single fibres which was estimated from the distribution of fibre failure strains (Figure 5.9). Probability,  $P_f$ , was calculated using an estimator commonly used in application of the Weibull distribution:

$$P_f = (j - 0.5)/n \quad (5.9)$$

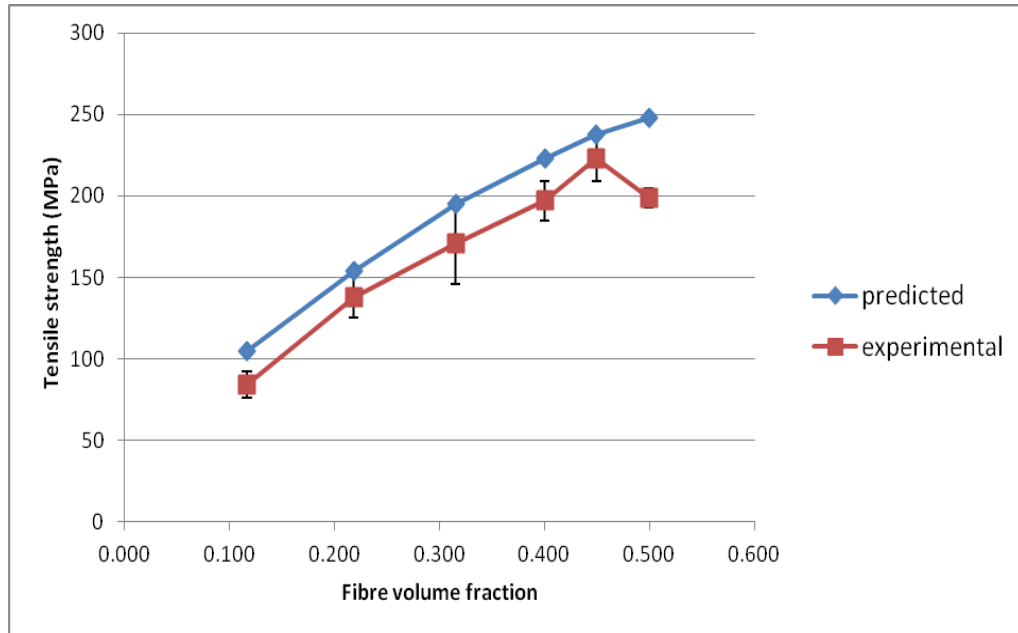
where  $n$  is the number of data points and  $j$  is the rank of the  $j$ -th data point



**Figure 5.9: Distribution of single harakeke fibre failure strains**

A cubic regression function was found to best fit the data. The lowest failure strain of 1.41% was found at the point that the probability was equal to 0. The stress on each tested fibre at the strain of 1.41% was obtained using the corrected stress-strain curves as mentioned previously (an example in Figure 6). The

average stress of all fibre specimens ( $\sigma_f$ ) at strain of 1.41% was 401 MPa (disregarding the lumen) and the average stress of all epoxy samples was 35.5 MPa. The corrected fibre stress of 680 MPa ( $401/0.59$ ) was substituted into Equation 5.8 to estimate tensile strength of aligned long harakeke/epoxy composites. The predicted and experimental strengths are presented in Figure 5.10. The prediction error varied from 5 to 24 % which is much improved from the Rule of Mixtures just taking account of porosity. It is possible that some of this difference could be accounted for by less than perfect interfacial bonding.



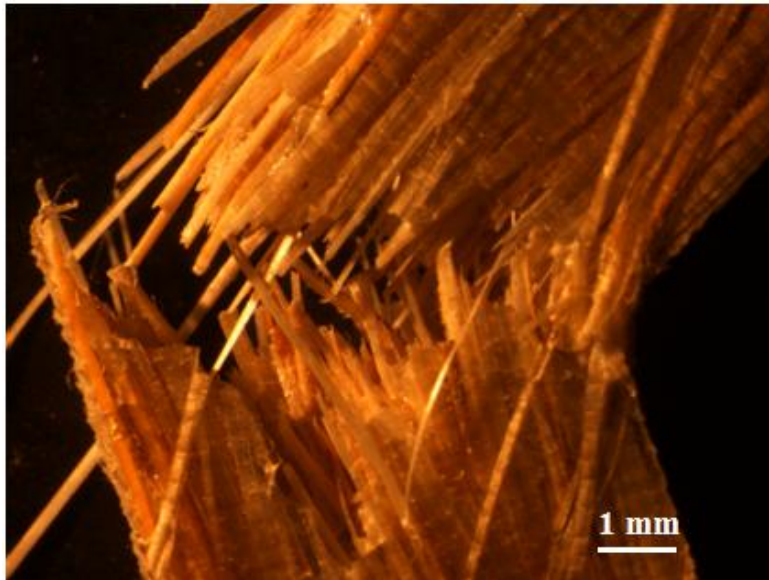
**Figure 5.10: Predicted and experimental strengths of harakeke/epoxy composites as a function of fibre volume fraction (applying tensile stress of the fibre and matrix at strains of 1.41%); each error bar corresponds to one deviation.**

Normally, the prediction error for Young's modulus and tensile strength of natural fibre composites using the conventional Rules of Mixtures increases at higher fibre volume fraction, but it did not happen to harakeke composites investigated in this work using the model taking account of porosity, supporting that the porosity

significantly affects the mechanical properties of aligned long harakeke composites, especially at high fibre volume fractions.

## 5.4 Impact strength

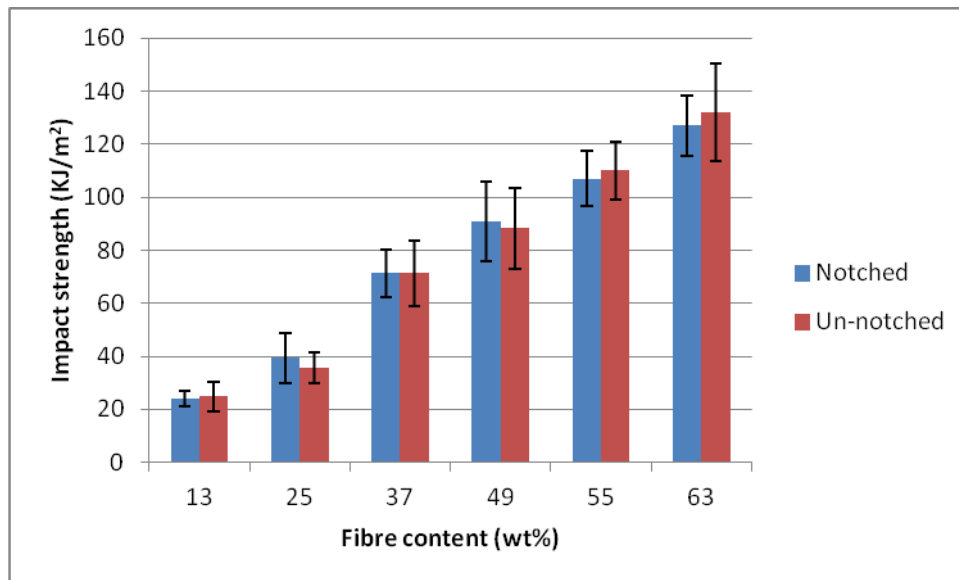
Micrographs of an impact tested aligned long harakeke composite sample is presented in Figure 5.11. As can be seen, samples were not broken into two pieces completely but some fibres linked two ends of the samples together. This mode of failure was associated with high energy absorption [141]. The micrograph also shows the fibre pullout due to the fracture of long fibres during impact testing



**Figure 5.11: Micrograph of an aligned long harakeke/epoxy composite sample after impact testing**

Figure 5.12 shows average impact strength for notched and un-notched samples of aligned long harakeke/epoxy composites as a function of fibre content. It can be clearly seen that the impact strengths for both samples increased linearly with fibre content. This was because more fibres and fibre/matrix interfaces exist on the crack path and therefore, more energy to break them was consumed.

Interestingly, the difference between impact strengths of notched and un-notched composite samples at different fibre contents was not significant as confirmed by the Student t-test, while the difference between those for neat epoxy was clearly,  $1.44 \text{ KJ/m}^2$  for the notched sample and  $9.19 \text{ KJ/m}^2$  for the un-notched. It suggests that epoxy matrix fracture might not contribute to impact strength of aligned long harakeke/epoxy composites. The dominant mechanism of the composite impact may be fibre fracture then pull out. Maximum impact strength of  $132 \text{ KJ/m}^2$  at fibre content of 63wt% is higher than any reported to date in the literature [29].

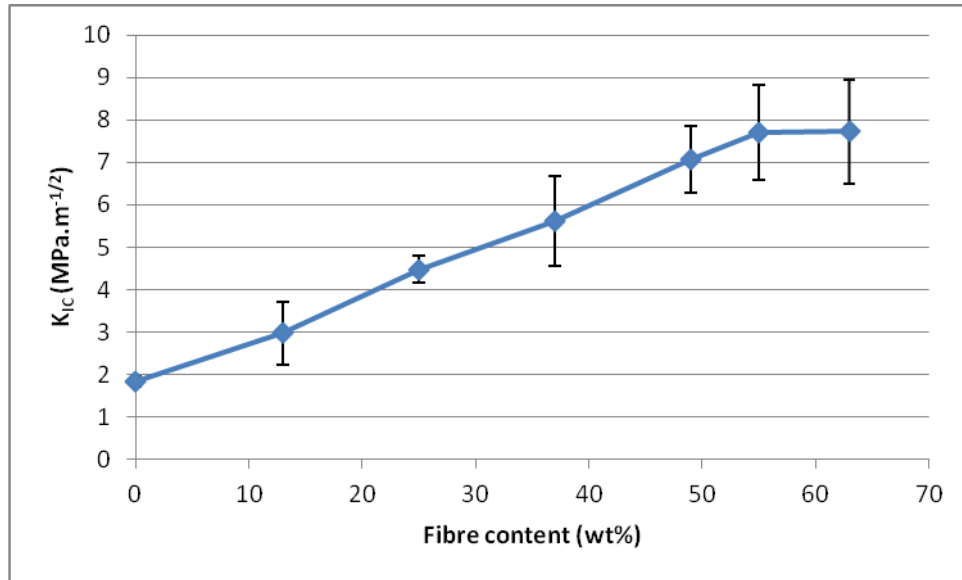


**Figure 5.12: Impact strength of aligned long harakeke/epoxy composites as a function of fibre content; each error bar corresponds to one deviation.**

## 5.5 Fracture toughness ( $K_{IC}$ )

Fracture toughness ( $K_{IC}$ ) of aligned long harakeke/epoxy composites as a function of fibre content is presented in Figure 5.13. . It can be seen that  $K_{IC}$  increased linearly as fibre content increased up to 53% and further addition of fibre did not improve  $K_{IC}$  of the composite.  $K_{IC}$  of  $7.69 \text{ MPa.m}^{-1/2}$  at a fibre content of 53% for aligned long harakeke/epoxy composites was 4.2 time higher than that of neat

epoxy and higher than any reported in the literature for natural fibre composites. High fracture toughness property of aligned long harakeke fibre reinforced epoxy composites could be due to a combination of high strength, fibre length and unidirectional orientation of harakeke fibre.



**Figure 5.13: Fracture toughness ( $K_{IC}$ ) of aligned long harakeke/epoxy composites as a function of fibre content; each error bar corresponds to one deviation.**

## 5.6 Chapter conclusions

The addition of aligned long harakeke fibre was found to significantly enhance the tensile and flexural properties of epoxy. The tensile properties, which were comparable to those of other cellulose based fibre composites, show the potential of harakeke fibre used in composites. Lumen volume in harakeke fibre is significant and must be considered to calculate tensile strength and Young's modulus of fibre and porosity of the composites. The model developed for predicting composite strength based on the assumption that composites fail when fibres with the lowest failure strains failed and considering the effect of porosity,



could be used to predict the tensile strength of aligned long harakeke fibre (or similar fibres) composites.

## **Chapter Six: Aligned short harakeke-hemp/epoxy hybrid biocomposites**

### **6.1 Introduction**

Short harakeke and hemp fibres treated with 5%NaOH/2%Na<sub>2</sub>SO<sub>3</sub> were incorporated in a low viscosity epoxy resin to produce hybrid biocomposites. Mechanical properties including tensile, flexural, impact and fracture toughness as functions of fibre lay-up as well as weight ratio between harakeke and hemp were assessed. The hybrid effects were also discussed. In this chapter, the words “flax” and “harakeke” are used interchangeably for ease of abbreviation to “F” for flax or harakeke and “H” for hemp.

### **6.2 Experimental**

#### **6.2.1 Materials**

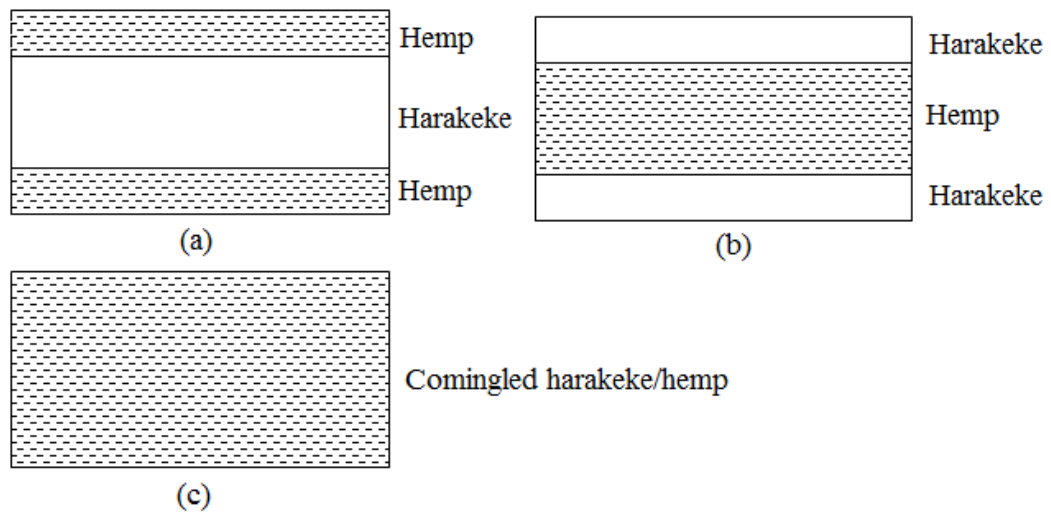
Short harakeke and hemp fibres digested with 5%NaOH/2%Na<sub>2</sub>SO<sub>3</sub> as detailed in Chapter 3 were used as the reinforcement. The matrix was a low viscosity epoxy system comprised of Nuplex resin R180 and Nuplex standard hardener H180 (mixing ratio 5:1 by weight).

#### **6.2.2 Methods**

##### ***6.2.2.1 Composite manufacture***

Aligned harakeke and hemp fibre sheets with an areal weight of 105 g/m<sup>2</sup> were prepared using DSF as described in Chapter 4. Hybrid biocomposites were manufactured using the same compression moulding and curing procedure used to produce short harakeke composites detailed in Section 4.2.2.3. Hybrid biocomposites with different lay-ups including sandwich structures

hemp/flax/hemp (HFH) and flax/hemp/flax (FHF) and comingled flax/hemp (FH11) as shown in Figure 6.1 were prepared. For sandwich hybrid composites, 8 DSF mat layers of harakeke fibre combined with 8 DSF mat layers of hemp fibre while comingled hybrid composites was made up of 16 mat layers. The total fibre weight fraction was 0.45 and weight ratio between two types of fibres was 1:1 or relative harakeke fibre content of 50%. Extra comingled hybrid biocomposites with different relative harakeke fibre contents of 25% and 75% were also prepared.



**Figure 6.1: Different lay-up of hybrid composites (a) FHF, (b) HFH, (c) HFHFH**

#### **6.2.2.2 Composite testing**

Composite densities were conducted using Archimedes as described in Section 4.2.2.6. Mechanical properties of hybrid biocomposites were carried out using methods detailed in Section 4.2.2.

## 6.3 Results and discussion

### 6.3.1 Physical properties of harakeke, hemp and hybrid composites and normalisation of composite properties

Physical properties of harakeke-only, hemp-only and hybrid composites including composite density, fibre weight fraction, fibre volume fraction and porosity fraction are tabulated in Table 6.1. There were small differences in fibre content of the different composites due to different amounts of different resin escaping from the mould when pressing during composite manufacture, resulting in different fibre volume fractions. It can also be seen in Table 6.1 that sandwich hybrid composites possessed higher porosity than the others. This might be due to air trapped in the interlaminar regions between harakeke and hemp layers.

**Table 6.1: Physical properties of harakeke, hemp and hybrid composites**

Sample	Wt%	$W_f$	$\rho_c$ (g/cm <sup>3</sup> )	$V_f$	$\rho_{ct}$ (g/cm <sup>3</sup> )	$V_p$
<b>F</b>	45.6	0.456	1.166 (0.04)	0.349	1.287	9.383
<b>FHF</b>	45	0.45	1.155 (0.011)	0.341	1.284	10.029
<b>HFH</b>	47.6	0.476	1.162 (0.010)	0.363	1.292	10.041
<b>FH11</b>	43.9	0.439	1.174 (0.031)	0.339	1.283	8.475
<b>FH13</b>	48	0.48	1.176 (0.024)	0.371	1.294	9.142
<b>FH31</b>	43	0.43	1.153 (0.014)	0.326	1.278	9.788
<b>H</b>	45.6	0.456	1.179 (0.023)	0.353	1.288	8.454

The comparison of properties between the composites should be conducted at the same fibre volume fraction. In actual fact, it was virtually impossible to produce composites with the same fibre volume fraction using compression moulding. Hence, a method of normalisation to normalise composite properties to those at a standardised fibre volume fraction was used. Within a small range of fibre volume fraction, properties for each type of composite were assumed to obey the Rule of Mixtures. Normalised properties were calculated by combining Equations 6.1 and 6.2:

$$P_{ce} = (k_1 k_2 P_f - P_m) V_{fe} + P_m \text{ or } P_{ce} - P_m = (k_1 k_2 P_f - P_m) V_{fe} \quad (6.1)$$

$$P_{cn} = (k_1 k_2 P_f - P_m) V_{fn} + P_m \text{ or } P_{cn} - P_m = (k_1 k_2 P_f - P_m) V_{fn} \quad (6.2)$$

where

P and V are property and fibre volume fraction, respectively;  $k_1$  and  $k_2$  are fibre orientation factor and fibre length factor, respectively; subscripts c, f, m, e, n denote composite, fibre, matrix, experimental and normalised, respectively.

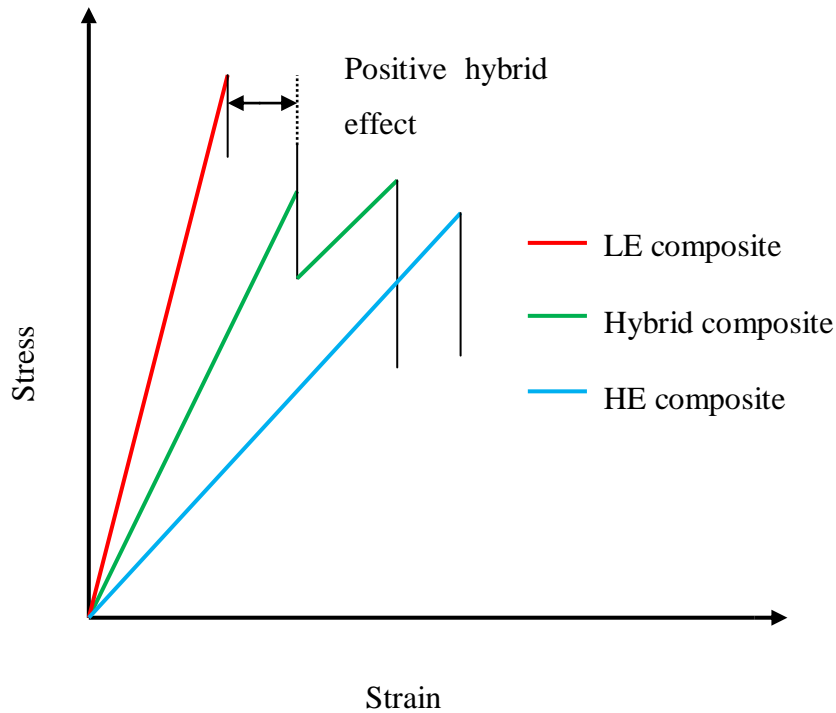
Dividing Equation 6.2 by Equation 6.1 gives

$$(P_{cn} - P_m) / (P_{ce} - P_m) = V_{fn} / V_{fe} \text{ or } P_{cn} = V_{fn} / V_{fe} (P_{ce} - P_m) + P_m \quad (6.3)$$

Such that the normalised values for composite properties can be calculated as experimental fibre volume fractions, experimental composite and epoxy properties were known. The average fibre volume fraction of all composites (0.35) in Table 6.1 was used as the standardised fibre volume fraction ( $V_{fn}$ ) to which properties were normalised. Composite properties presented in the following sections in this chapter are normalised values.

### 6.3.2 The hybrid effect

For a hybrid composite with two types of fibres, the fibre type with lower breaking elongation is often termed as the LE fibre and the other type with higher breaking elongation is designated as the HE fibre. As mentioned in Chapter 2, there are two definitions of the hybrid effect; one is based on the failure strain (FS) of fibre and the other is based on the Rule of Mixtures (ROM). In this thesis, these were called the FS hybrid effect and ROM hybrid effect, respectively. The FS hybrid effect is illustrated in Figure 6.2.

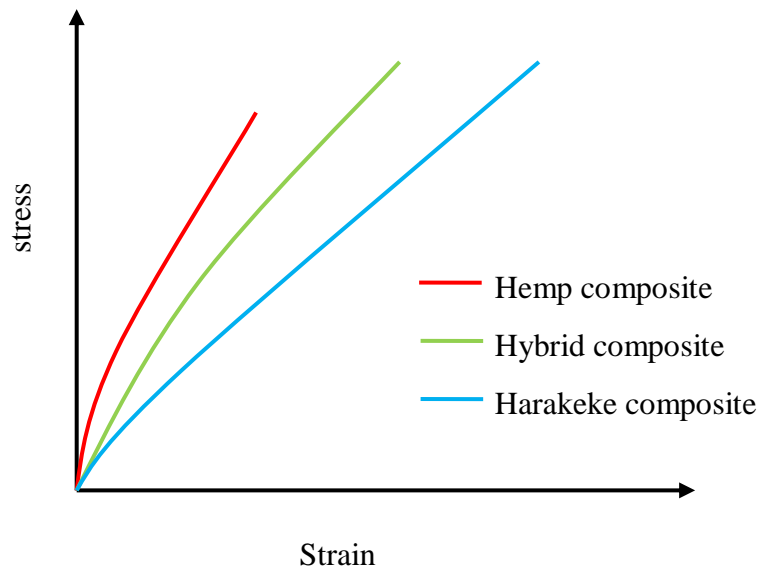


**Figure 6.2: Illustration of the definition of the hybrid effect based fibre failure strain.**

In a synthetic fibre hybrid composite, there are two distinct stages of fracture; the initial one corresponds to the failure of the LE fibre and the final one when the hybrid composite fails. The enhancement of hybrid composite strain at initial fracture compared to failure strain of LE fibre composite is called the FS hybrid

effect. The existence of the FS hybrid effect for synthetic fibre hybrid composites is now well established, but not thoroughly understood [11].

The typical stress-strain curves of harakeke-only, hemp-only and hybrid composites are shown in Figure 6.3. It can be seen that, for harakeke/hemp hybrid composites, only fibre fracture but not initial fracture was observed and therefore the FS hybrid effect was not observed. Hence, only the ROM hybrid effect was further assessed for properties of harakeke/hemp hybrid composites.



**Figure 6.3: Typical stress-strain curves of harakeke, hemp and hybrid composites.**

The properties of the harakeke/hemp hybrid composites can be predicted using the Rule of hybrid Mixtures [142]

$$P_{Hb} = P_F V_F + P_H V_H \quad (6.4)$$

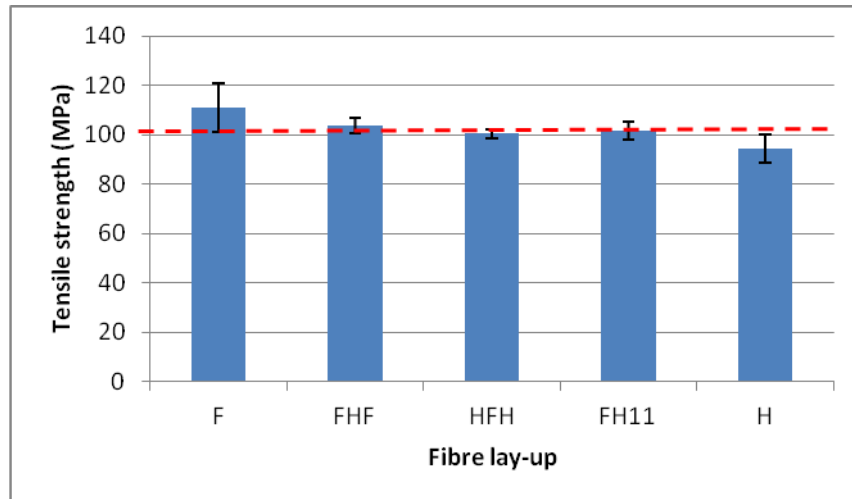
where  $P$  is the property to be investigated,  $V$  is relative hybrid fibre volume fraction, subscripts Hb, F and H denote hybrid, flax or harakeke and hemp, respectively.

$$V_F + V_H = 1 \quad (6.5)$$

A positive or negative ROM hybrid effect is defined as a positive or negative deviation of a certain mechanical property from the hybrid Rule of Mixtures.

### 6.3.3 Composite tensile properties

Figures 6.4 and 6.5 show the strength and Young's modulus, respectively, of hybrid composites as well as harakeke-only and hemp-only composites as a function of fibre lay-up. Harakeke-only composites (F) had higher strength but lower stiffness than hemp-only composites. This could be explained by the fact that the harakeke fibre was stronger but possessed lower stiffness compared to hemp fibre (see Table 3.5).

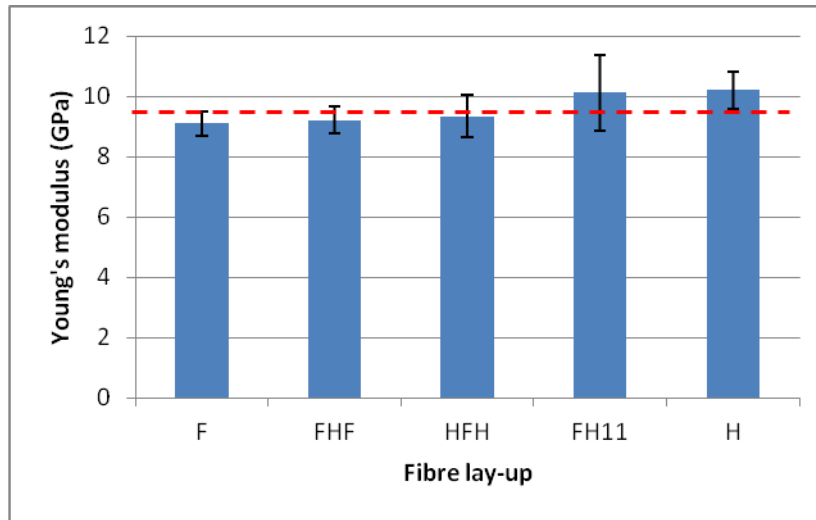


**Figure 6.4: Composite tensile strength versus fibre lay-up including a ROM line. Error bars indicate one standard deviation.**

**Figure 6.4** shows that tensile strengths of hybrid lie between those of harakeke-only composites and hemp-only composites. The tensile strength appears possibly



to be higher when harakeke was used as the skin material and hemp as the core material (FHF) compared to when hemp was used as the skin and harakeke used as the core (HFH). The tensile strength of the comingled hybrid composites (FH11) is almost the same as that of the FHF composites and higher than that of HFH composites. However, the difference between tensile strengths of hybrid composites was not statistically significant as confirmed by ANOVA analysis.

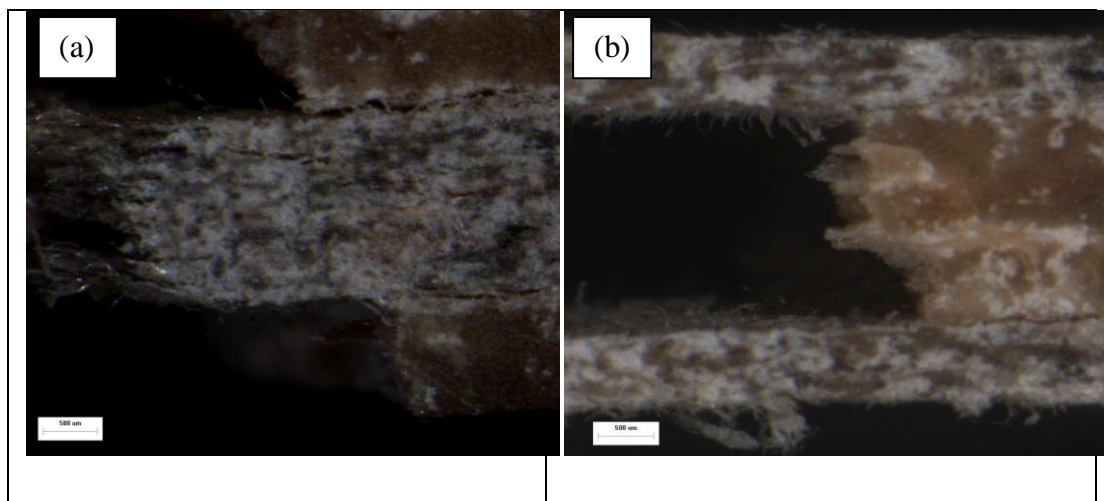


**Figure 6.5: Composite Young's modulus versus fibre lay-up including a ROM line. Error bars indicate one standard deviation.**

As can be seen in Figure 6.5, Young's moduli of hybrid composites were between those of hemp-only and harakeke-only composites with the highest value for FH11. Young's modulus of natural fibre composites, in the literature, was found to decrease as porosity in composites increased [127]. As shown in Table 6.1, porosity in FH11 hybrid composites is lower than that of sandwich composites which could explain why FH11 hybrid composites possessed the highest Young's modulus for hybrid composites. As discussed above, higher porosity in sandwich hybrid composites was likely to be due to trapped air at interlaminar regions between harakeke and hemp layers. The high porosity at the interlaminar regions could reduce the stress transfer between hemp and harakeke parts in sandwich

hybrid composites, which could possibly cause interlaminar delamination between harakeke and hemp layers in sandwich hybrid composites as shown in Figure 6.6, and result in reduction of their stiffness.

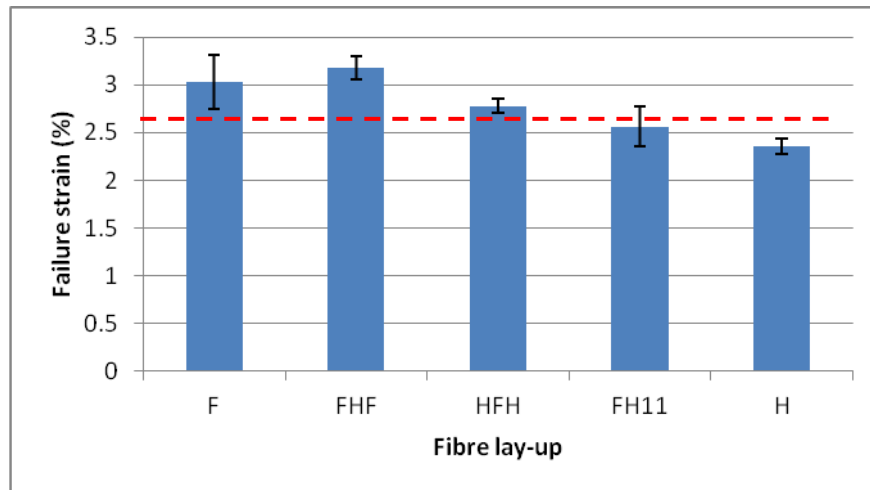
Tensile strength and Young's modulus of harakeke/hemp hybrid composites appeared to obey the Rule of Mixtures as the broken lines determined based on the Rule of Mixtures lie within their data spread. In other words, no ROM hybrid effect was observed.



**Figure 6.6: Side views of failed tensile coupons of sandwich hybrid composites showing interlaminar delamination between harakeke and hemp layers: (a) FHF composite and (b) HFH composite.**

Tensile failure strains of the composites are presented in Figure 6.7. It can be seen that, the failure strain of harakeke-only composites is higher than that of hemp-only composites which is likely to be due to higher failure strain of harakeke fibre (see Tables 3.3 and 3.4). Failure strain of FHF hybrid composite appears to be the highest of all. However, the difference between it and harakeke-only composite failure strain was not significant as confirmed by the Student t-test. Failure strain of FH11 hybrid composites was the lowest among the hybrid composites but higher than that of hemp-only composites. Interlaminar delamination in sandwich

hybrid composites might enhance their tensile failure strain. The high failure strain of FHF composites which have harakeke at the outer layers indicates that material at the outer layer of sandwich composites possibly affects tensile failure strain of the hybrid composites.

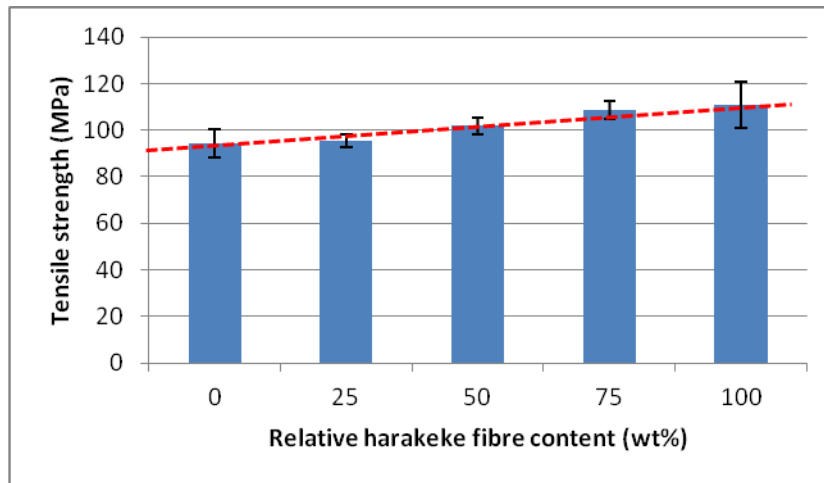


**Figure 6.7: Failure strain versus fibre lay-up including a ROM line. Error bars indicate one standard deviation.**

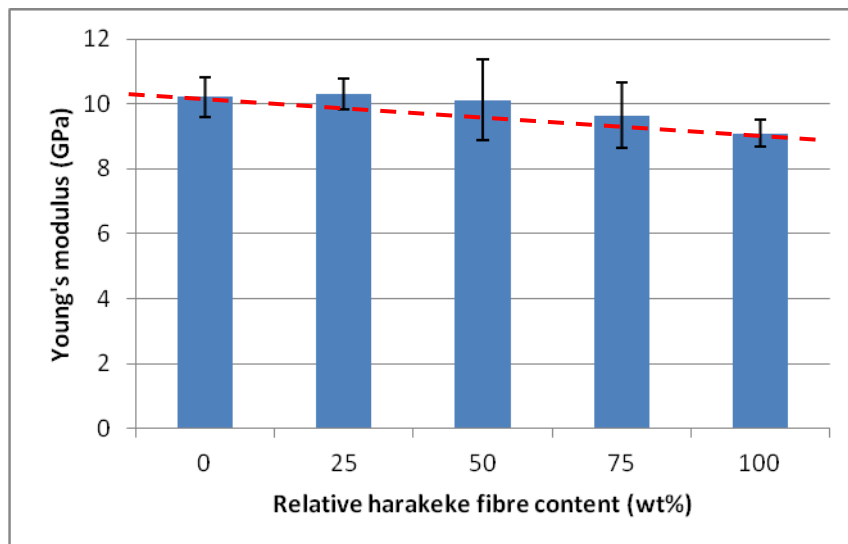
The ROM line is within the lower and upper limit values shown for standard deviation of failure strain of FH1, while it lies below the lower limit of FHF and HFH composites. This indicates that failure strain of comingled fibre hybrid composites followed the Rules of Mixtures, while a positive ROM hybrid effect was observed for sandwich hybrid composites. The positive hybrid observed for sandwich hybrid composites was possibly due to the interlaminar delamination between harakeke and hemp fibre layers. In the case of comingled fibre hybrid composites, harakeke and hemp fibre were intimately mixed during fibre mat production using the DSF giving a uniform reinforcement and in the composites, no interlaminar planes formed between harakeke and hemp fibres as for sandwich hybrid composites, and therefore no interlaminar delamination occurred. This

could explain why the ROM hybrid effect was not observed for FH11 hybrid composites.

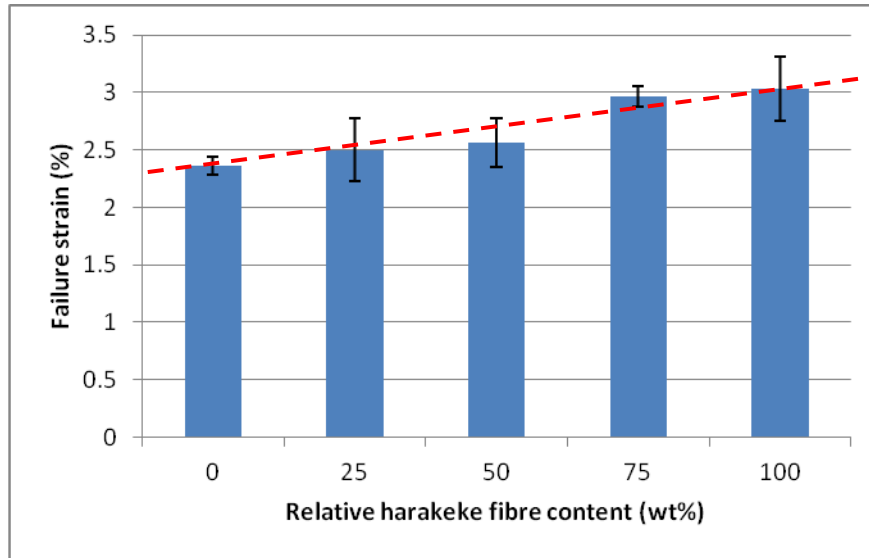
The tensile strength, Young's modulus and failure strain of hybrid composites with different harakeke proportions are presented in Figures 6.8, 6.9 and 6.10, respectively. Tensile strength and failure strain increased while Young's modulus decreased as harakeke fibre content increased following the Rule of Mixtures.



**Figure 6.8: Tensile strength versus proportion of harakeke fibre including a ROM line. Error bars indicate one standard deviation.**



**Figure 6.9: Young's modulus versus proportion of harakeke fibre including a ROM line. Error bars indicate one standard deviation.**



**Figure 6.10: Failure strain versus proportion of harakeke fibre including a ROM line. Error bars indicate one standard deviation.**

#### 6.3.4 Flexural properties

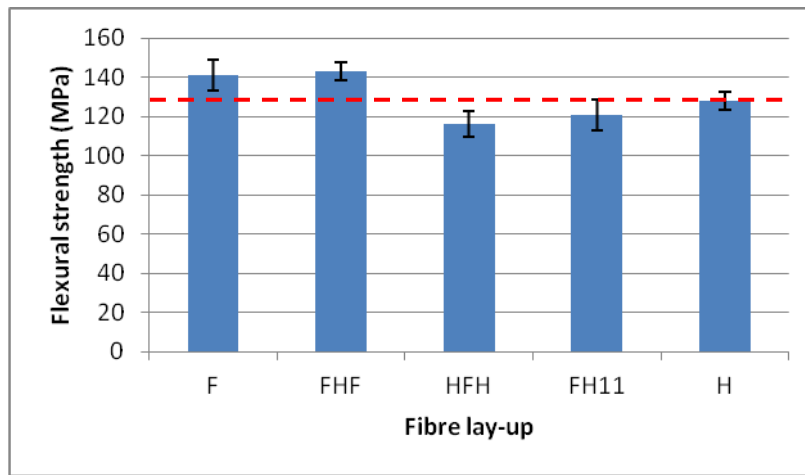
Flexural samples of non-hybrid and hybrid composites did not break completely into two parts, but cracks appeared at the outer fibre layers far away from the neutral axis, similar to the behaviour of aligned short harakeke fibre composites (see Figure 4.6).

Flexural strength and flexural modulus of non-hybrid composites and hybrid composites are presented in Figures 6.11 and 6.12, respectively. It can be seen that flexural strength of harakeke-only composites was higher than that of hemp-only composites while Young's modulus had the opposite trend, assumed to be due to harakeke fibre being stronger but having lower stiffness than hemp fibre.

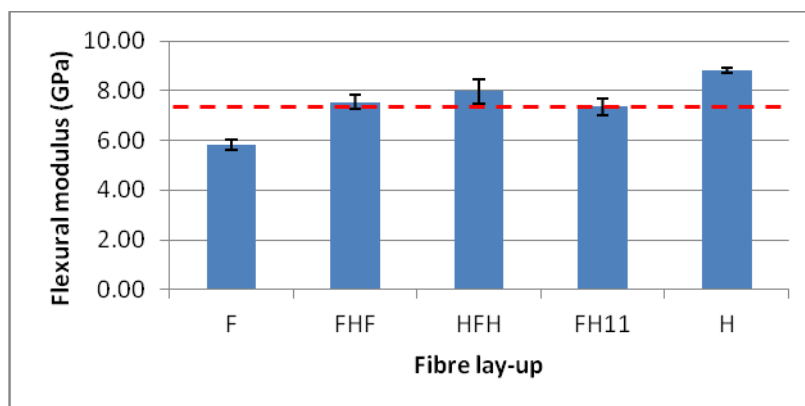
FHF and HFH sandwich hybrid composites were found to be higher and lower, respectively compared to FH11 which can be explained as being due to the stronger layers (harakeke) have high second moment of area when they are the

outer layers, and thus no obvious hybrid effect was observed. The ROM line falls within the spread of data for FH11 giving no clear evidence of a hybrid effect as for tensile strength.

Flexural moduli of hybrid composites were found to be higher than that for harkeke-only composites but lower than that for hemp-only composites following the Rule of Mixtures, and their differences were not statistically different as confirmed by ANOVA analysis.

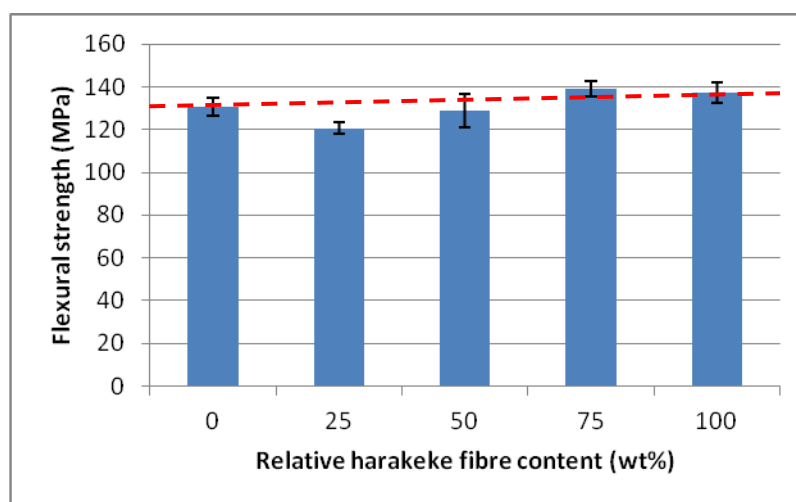


**Figure 6.11: Flexural strength versus fibre lay-up including a ROM line. Error bars indicate one standard deviation.**

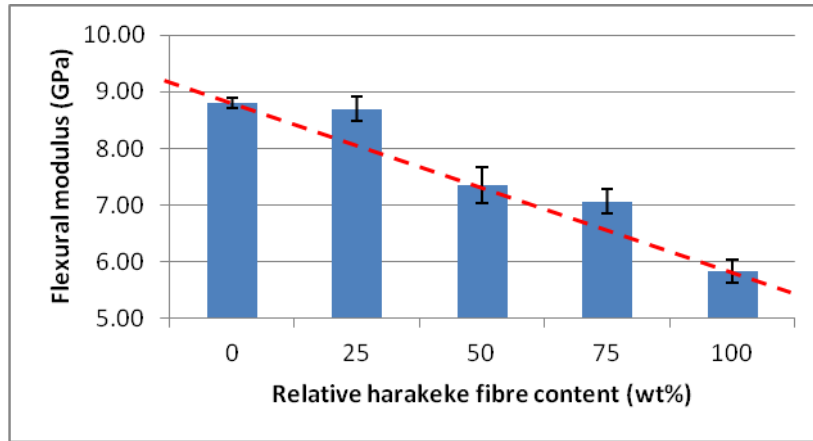


**Figure 6.12: Flexural modulus versus fibre lay-up including a ROM line. Error bars indicate one standard deviation.**

The flexural strength and flexural modulus of comingled hybrid composites as a function of harakeke fibre content are presented in Figures 6.13 and 6.14, respectively. The flexural strength increased as harakeke fibre content increased, while the modulus decreased as harakeke fibre content increased as expected. A negative ROM hybrid effect and a positive ROM hybrid effect were observed for the flexural strength at a harakeke fibre content of 25% and 75%, respectively. This is consistent with the trend observed for flexural strength of kapok/sisal fabric reinforced polyester hybrid composites at kapok fibre contents of 25% and 75%. [143]. However, a positive hybrid effect have also been observed for flexural strength of short banana/sisal fibre hybrid composites [104] and agreement with ROM as well as a positive effect was observed for sisal/glass fibre reinforced unsaturated hybrid composites depending on the total volume fraction of fibres [144].



**Figure 6.13: Flexural strength versus proportion of harakeke fibre including a ROM line. Error bars indicate one standard deviation.**



**Figure 6.14: Flexural modulus versus proportion of harakeke fibre including a ROM line. Error bars indicate one standard deviation.**

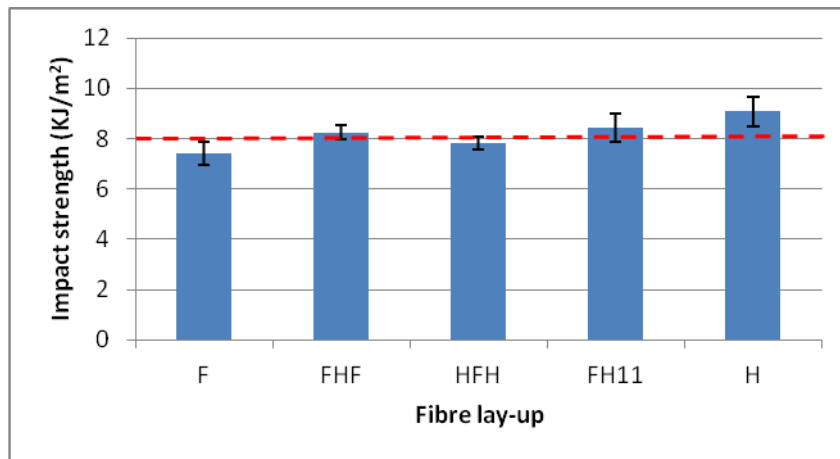
A positive hybrid effects was observed for flexural modulus of comingled harakeke/hemp fibre composites at different relative harakeke fibre contents with an exception at the relative harakeke fibre content of 50% as shown in Figure 6.14. In the literature, a positive effect was also observed for flexural moduli of kapok/sisal fibre fabric reinforced unsaturated polyester hybrid composites [143], short banana/sisal fibre reinforced unsaturated polyester hybrid composites [104] and short sisal/glass fibre reinforced unsaturated polyester hybrid composites [144] at different relatives fibre contents. Indeed, a positive hybrid effect for flexural modulus of natural fibre hybrid composites has seemed to be observed consistently in the literature. Fibre dispersion has been found to be higher in hybrid composites compared to non-hybrid composites [46], resulting in an increased fibre wetting as well as physical adhesion between the fibre and the matrix [104] which could improve flexural modulus of the hybrid composites.

### 6.3.5 Impact strength

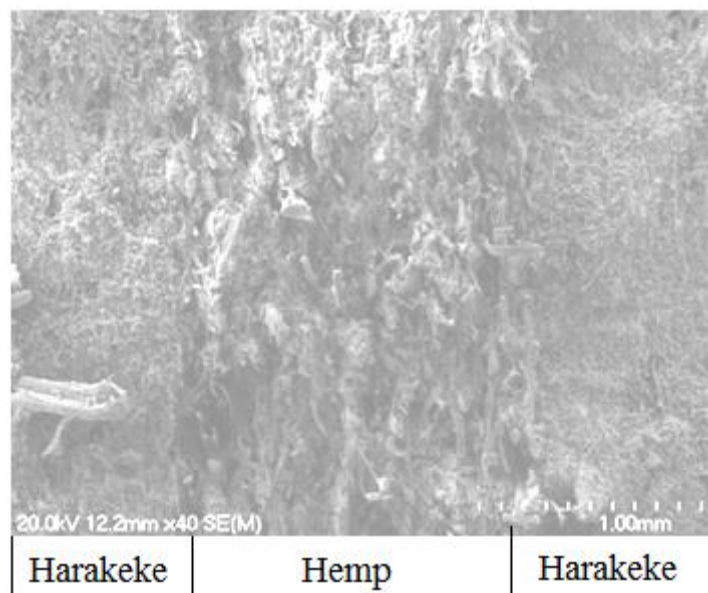
Average values of impact strengths of non-hybrid and hybrid composites are presented in Figure 6.15. As can be seen, the impact strength for hemp was higher than that for harakeke. This was surprising since harakeke fibre was stronger and



had a higher failure strain than hemp (see Tables 3.3, 3.4 and 3.5), and as such its composites were expected to have higher impact strength than hemp composites. Matrix cracking, fibre failure, fibre/matrix debonding and fibre pull-out are the main mechanisms contributing to impact failure of short fibre composites [145]. Of these, increased fibre pull-out has been found to lead to increased impact [145; 146].

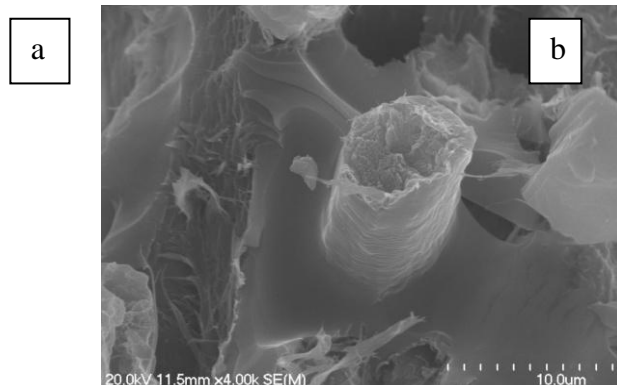


**Figure 6.15: Impact strength versus fibre lay-up including a ROM line. Error bars indicate one standard deviation.**



**Figure 6.16: A SEM image of a fracture surface of FHF hybrid composite failed during impact testing.**

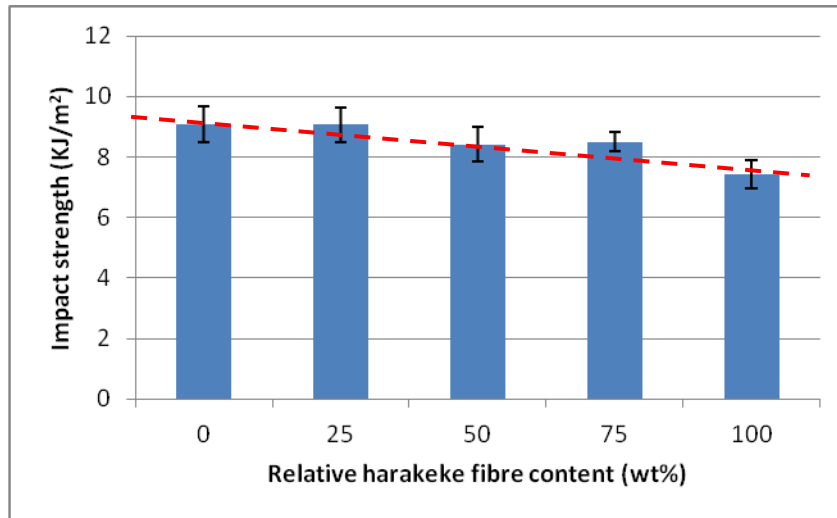
Figure 6.16 shows a fracture surface of an FHF hybrid composite failed during impact testing. The surfaces of the harakeke sections at the sides are flatter than that of the hemp section in the middle. This indicates that more pull-out of hemp fibres occurred. The interfacial bonding appeared to be better for harakeke fibre than hemp fibre as shown in **Figure 6.17**. This is consistent with discussion in Chapter 3 on the surfaces of harakeke fibres being rougher than that of hemp fibres and so providing better interfacial bonding and therefore giving shorter critical fibre length for harakeke, resulting in less pull-out of harakeke fibres. Moreover, the diameters of hemp fibres were greater than that for harakeke, resulting in the critical fibre length of hemp fibres being greater than that of harakeke fibres and giving longer pull-out hemp fibres.



**Figure 6.17: SEM images showing fibre/matrix interfacial bonding (a) hemp composite and (b) harakeke composite.**

Impact strengths of all hybrid composites with different fibre lay-up (see Figure 6.15) were found to be between those of harakeke and hemp composites and the difference between them was not significant as confirmed by ANOVA analysis. The impact strengths of hybrid composites obeyed the Rule of Mixtures with no ROM hybrid effect observed.

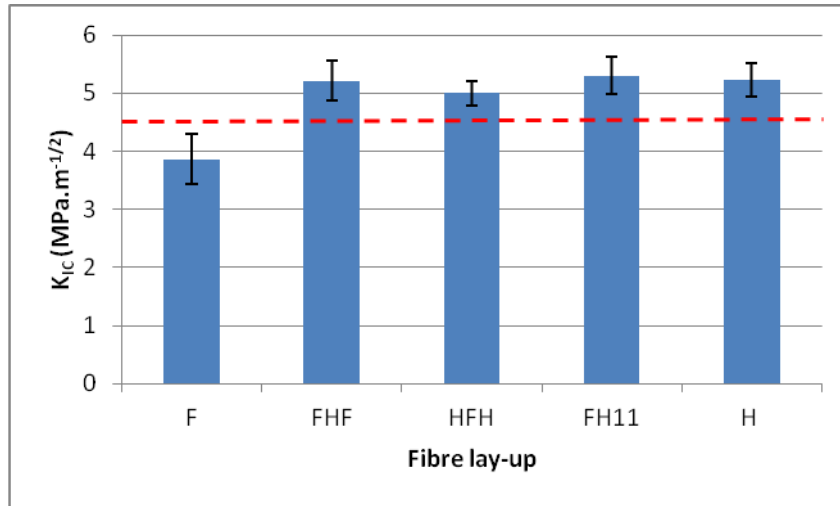
Impact strengths of comingled fibre hybrid composites as a function of harakeke fibre are presented in Figure 6.18. As can be seen, the impact strength decreased as the harakeke fibre content increased following the Rule of Mixtures.



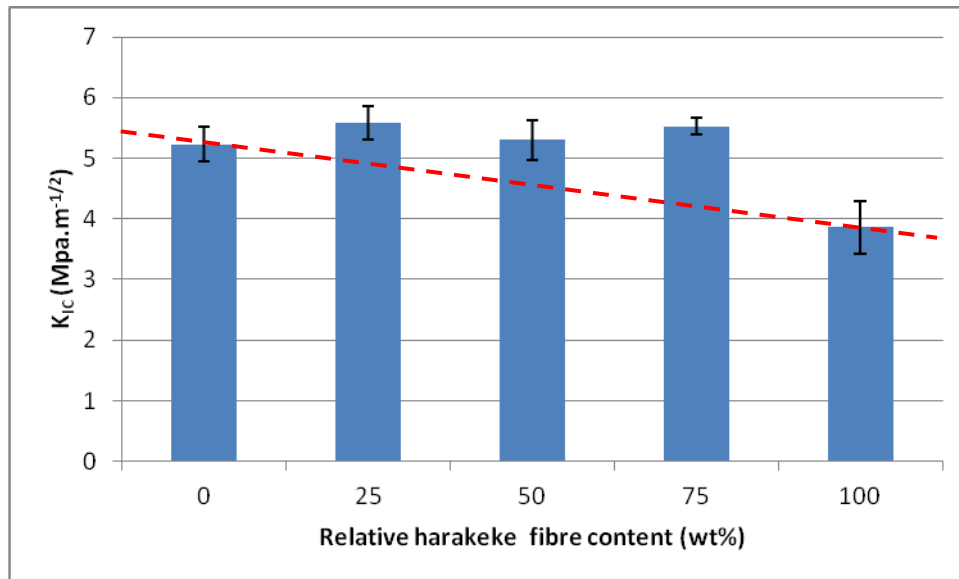
**Figure 6.18: Impact strength versus proportion of harakeke fibre including a ROM line. Error bars indicate one standard deviation.**

### 6.3.6 Fracture toughness ( $K_{IC}$ )

Average values of fracture toughness ( $K_{IC}$ ) of non-hybrid and hybrid composites are presented in Figure 6.19. It indicates that hemp composites were tougher than harakeke composites. Fracture toughness of non-hybrid composites has been found generally to be well correlated with Charpy V-notched impact strength [147], and therefore, factors affecting the impact strength can be assumed to influence the fracture toughness. Hence, factors including fibre length and interfacial bonding discussed for the impact strength can be used to explain why  $K_{IC}$  of hemp composites was higher than that of harakeke composites.



**Figure 6.19: Fracture toughness  $K_{IC}$  versus fibre lay-up including a ROM line. Error bars indicate one standard deviation.**



**Figure 6.20: Fracture toughness  $K_{IC}$  versus proportion of harakeke fibre including a ROM line. Error bars indicate one standard deviation.**

$K_{ICs}$  of the hybrid composites were higher than for harakeke composites and similar to that of hemp composites. According to ANOVA analysis, there was no significant difference between  $K_{ICs}$  of the hybrid composites. Interestingly,  $K_{IC}$  of the hybrid composites did not obey the Rule of Mixtures as impact strength did, but a positive hybrid effect was observed. HE fibres in the literature have been found to act as crack arresters in hybrid composites as HE fibres have a higher

failure strain, they can bridge the cracks formed by the broken LE fibres [148]. This finding helps to explain why the hybrid effect was observed for fracture toughness of the harakeke/hemp hybrid, of which, harakeke fibres played the role of HE fibres. It is also helpful to explain the pronounced hybrid effect at low LE fibre content as shown in Figure 6.20.

## **6.4 Chapter conclusions**

Tensile properties, impact strength and fracture toughness of aligned short harakeke/hemp hybrid composites were not influenced by fibre lay-up while flexural properties depended more on the outer layers of the composites.

For applications where a number of properties are important, a combination of harakeke and hemp fibres could be used to improve the balance between properties; harakeke fibre could increase tensile and flexural strength whilst hemp fibre could increase Young's modulus, flexural modulus, impact strength and fracture toughness of hybrid biocomposites

In this work, the hybrid effect defined based on fibre failure strain was not observed due to undetermined initial fibre failure strain in hybrid composites. Based on the Rule of Mixtures, a positive ROM hybrid effect was observed for flexural modulus of comingled fibre hybrid composites at different relative harakeke fibre contents and fracture toughness of hybrid composites with different fibre lay-up whilst the trend for flexural was irregular as a negative ROM hybrid effect was observed at a relative harakeke fibre content of 25% and a positive ROM effect at the content of 75%. In contrast, tensile and impact properties were found to obey the Rule of Mixtures.

## **Chapter Seven: Aligned long harakeke-hemp fibres/epoxy hybrid biocomposites**

### **7.1 Introduction**

In this work, aligned long harakeke and hemp fibres were incorporated into epoxy resin to produce hybrid biocomposites. Tensile and flexural properties, impact strength and fracture toughness of the hybrid biocomposites with different fibre lay-up were evaluated. In this chapter, the words “flax” and “harakeke” are used interchangeably for ease of abbreviation to “F” for flax or harakeke and “H” for hemp

### **7.2 Experimental**

#### **7.2.1 Materials**

Long fibre bundles mechanically extracted from harakeke leaves were obtained from the Templeton Flax Mill, Riverton, New Zealand whilst retted hemp bast fibre was supplied by Hemcore, UK. Morphologies of these fibres were shown in **Figure 7.1**.



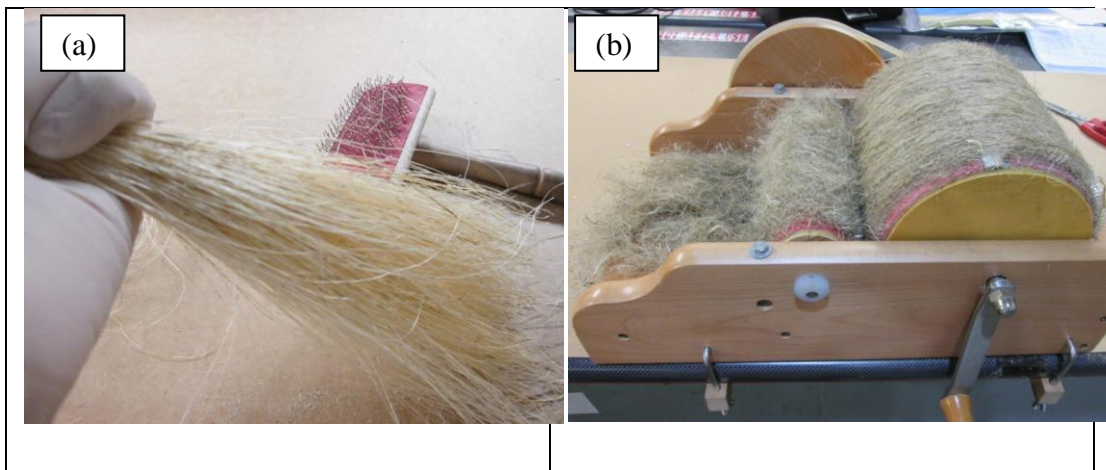
**Figure 7.1: (a) harakeke fibre bundles and (b) hemp fibres.**

A low viscosity epoxy system comprised of Nuplex resin R180 and Nuplex standard hardener H180 (mixing ratio 5:1 by weight) was used as the matrix.

## 7.2.2 Methods

### 7.2.2.1 Fibre mat preparation

Harakeke and hemp fibre were manually aligned using a brush and a manual carding machines, respectively, as shown in Figure 7.2. The fibres were then cut to fit a compression mould.



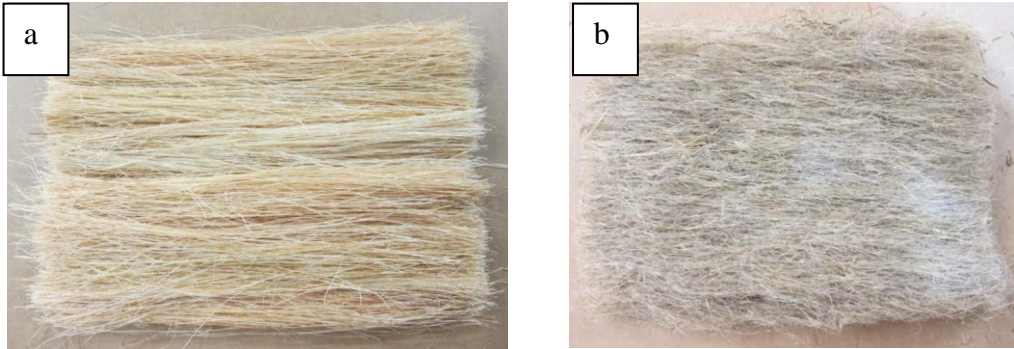
**Figure 7.2: (a) combed harakeke fibres using a brush and (b) carded hemp fibres using a manual carding machine.**

### 7.2.2.2 Composite manufacture

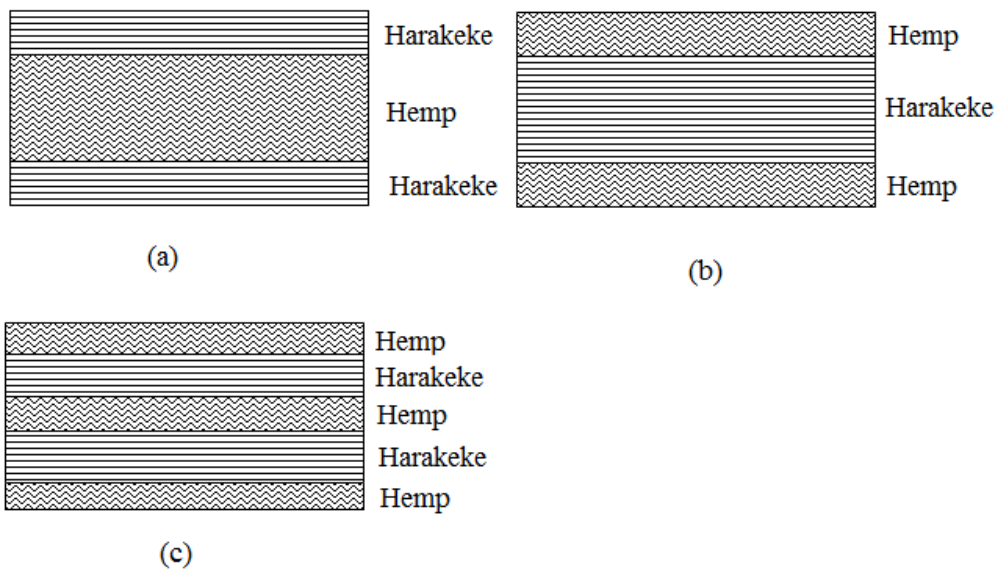
Aligned harakeke and hemp fibres shown in Figure 7.3 were oven dried overnight at 80°C and then hand laid into a simple rectangular mould lined with a Teflon sheet to form a fibre mat. Layers were arranged symmetrically with ordering of flax/hemp/flax (FHF), hemp/flax/hemp (HFH) and hemp/flax/hemp /flax/hemp (HFHFH) as shown in Figure 7.4 to prepare for hybrid composites. Mats of flax and hemp fibres were also prepared for flax-only (F) and hemp-only composites



(H), respectively. Composite manufacture followed the the process detailed in Section 5.2.2.1. The designed total fibre volume fraction was 0.4, and the volume ratio between harakeke and hemp fibres was 1:1.



**Figure 7.3: Aligned long fibre mats: (a) harakeke and (b) hemp**



**Figure 7.4: Different lay-up of hybrid composites (a) FHF, (b) HFH, (c) HFHFH**

### 7.2.2.3 Composite physical and mechanical testing

The measurement of tensile, flexural, fracture toughness and impact strength of composites as well as composite density was detailed in Chapter 5.



#### **7.2.2.4 Microscopy**

A WILD M3B stereo microscope fitted with a Nikon camera (Digital Sight DS-U1) was used to study composite sample surfaces and edges after flexural, fracture toughness and impact testing.

Tensile fracture surface morphology of composites was investigated using a Hitachi S4100 field emission scanning electron microscope (FESEM) operated at 5 kV. All samples were mounted on aluminum stubs using carbon tapes and then sputter coated with platinum to make them conductive prior to observation.

#### **7.2.2.5 Statistical analysis**

The Student's t-test and analysis of variance (ANOVA) were used to compare average strength of two or more different composites to confirm whether the difference between them was significant. The tests were conducted using Microsoft Excel 2010 software.

### **7.3 Results and discussion**

#### **7.3.1 Determining the hybrid effect**

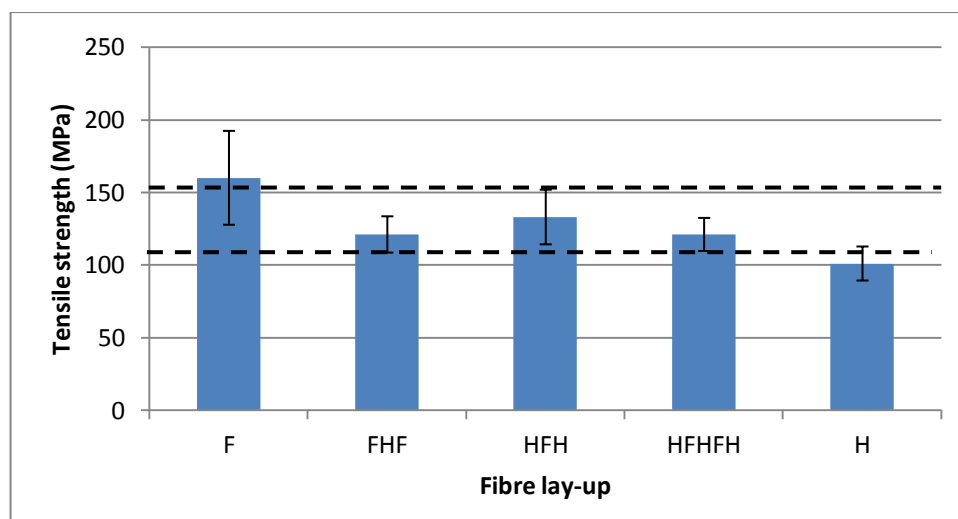
In this work, due to large variability of mechanical properties for aligned long harakeke-only and hemp-only fibre composites, lower bound and upper bound Rule of Mixtures (ROM) lines instead of an average ROM line were determined from lower limit and upper limit values of the properties for harakeke and hemp composites, respectively. Lower limit and upper limit values are calculated by subtracting and adding one standard deviation from and to an average value, respectively. A positive hybrid effect and negative effect will be observed for a hybrid composite if its tensile strength is above the upper bound ROM line and

below the lower bound ROM line, respectively whilst a property will obey the Rule of Mixtures if its value falls between the two lines.

### 7.3.2 Composite tensile testing results

The average tensile strengths for non-hybrid and hybrid composites are presented in Figure 7.5. It can be seen that the tensile strength for harakeke-only composites (F) was higher than that for hemp-only composites (H). Higher fibre tensile strength, longer fibre bundles and better fibre alignment for harakeke than hemp fibre could contribute to the higher tensile strength of harakeke composites. Tensile strengths of hybrid composites with different lay-up are found to be between those for harakeke-only and hemp-only composite following the Rules of Mixtures.

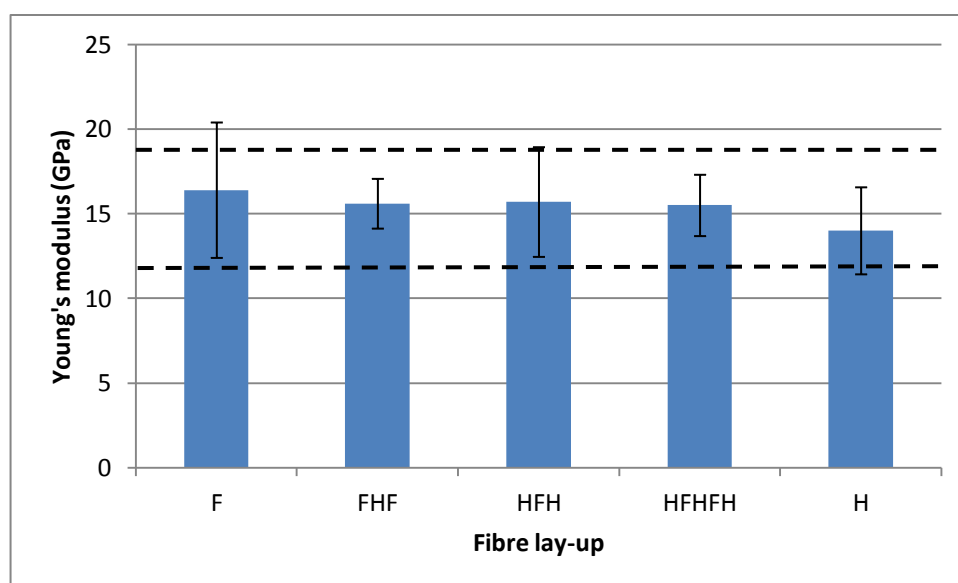
The tensile strength for sandwich hemp/flax/hemp (HFH) composites appeared to be higher than for the other hybrid composites, but the difference was not statistically significant as confirmed by single factor ANOVA analysis.



**Figure 7.5: Composite tensile strength versus fibre lay-up including lower and upper bound ROM lines. Error bars each denote  $\pm 1$  standard deviation.**

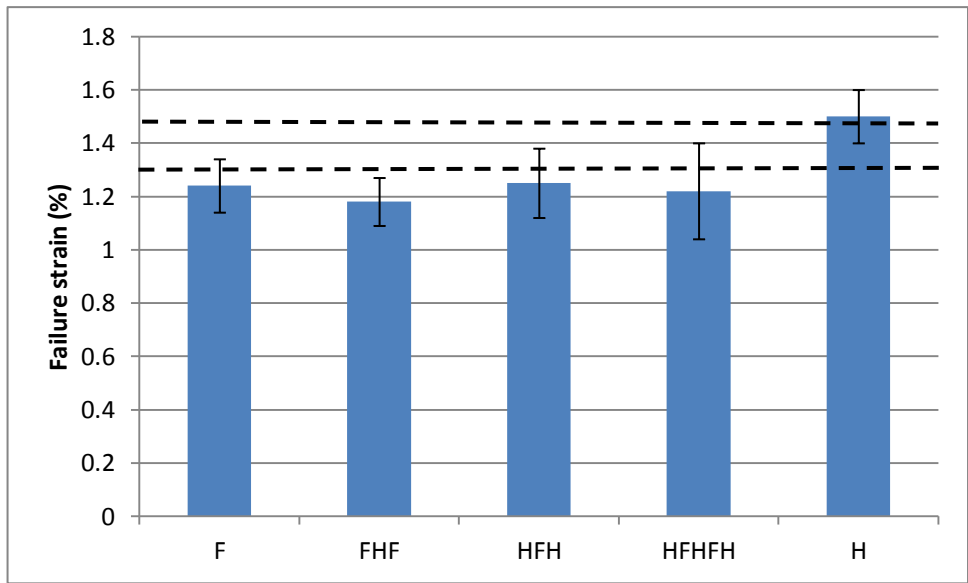
The average Young's moduli of non-hybrid and hybrid composites are presented in Figure 7.6. It can be seen that Young's modulus for harakeke-only composites was higher than for hemp-only composites, which could be due to true Young's modulus of harakeke fibre considering the effect of fibre lumens was higher than that of hemp fibre although measured Young's modulus for hemp fibre was greater. Fibre length and alignment also enhanced the Young's modulus of harakeke-only composites compared to hemp-only composites.

Young's moduli for hybrid biocomposites fell between those for harakeke-only composites and hemp-only composites following the Rules of Mixtures. According to ANOVA analysis, there was no statistically significant difference between Young's moduli for hybrid biocomposite with different lay-up.

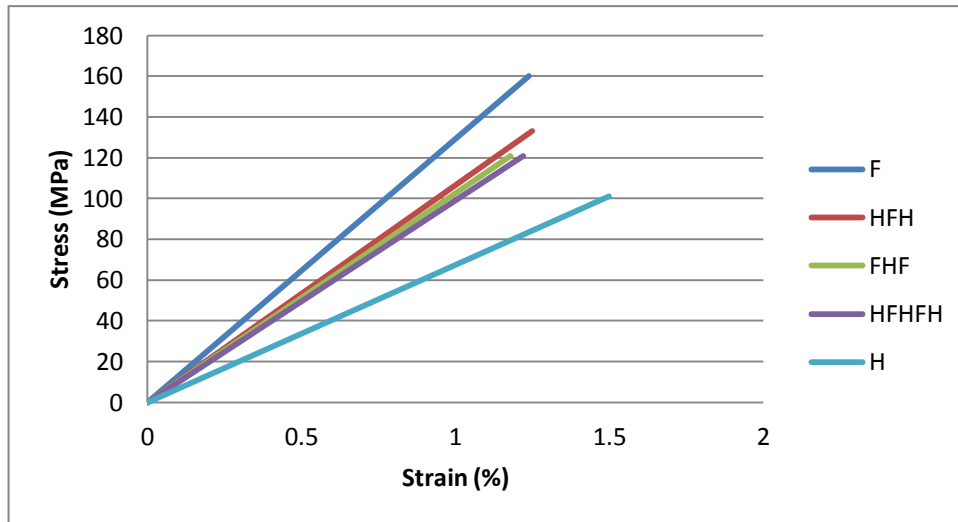


**Figure 7.6: Composite Young's modulus versus fibre lay-up including lower bound and upper bound ROM lines. Error bars each denote  $\pm 1$  standard deviation.**

Figure 7.7 presents the failure strain of non-hybrid composites and hybrid composites with different fibre lay-ups. The failure strain for harakeke-only composites appears to be lower than that for hemp-only composites. The failure strains for hybrid composites with different lay-up were similar to that for harakeke-only composite suggesting that hybrid composite failure was initiated by failure of harakeke fibres. Failure strains for hybrid composites are below the lower bound ROM line indicating that a negative ROM hybrid effect was observed.



**Figure 7.7: Composite failure strain versus fibre lay-up. Error bars each denote  $\pm 1$  standard deviation.**

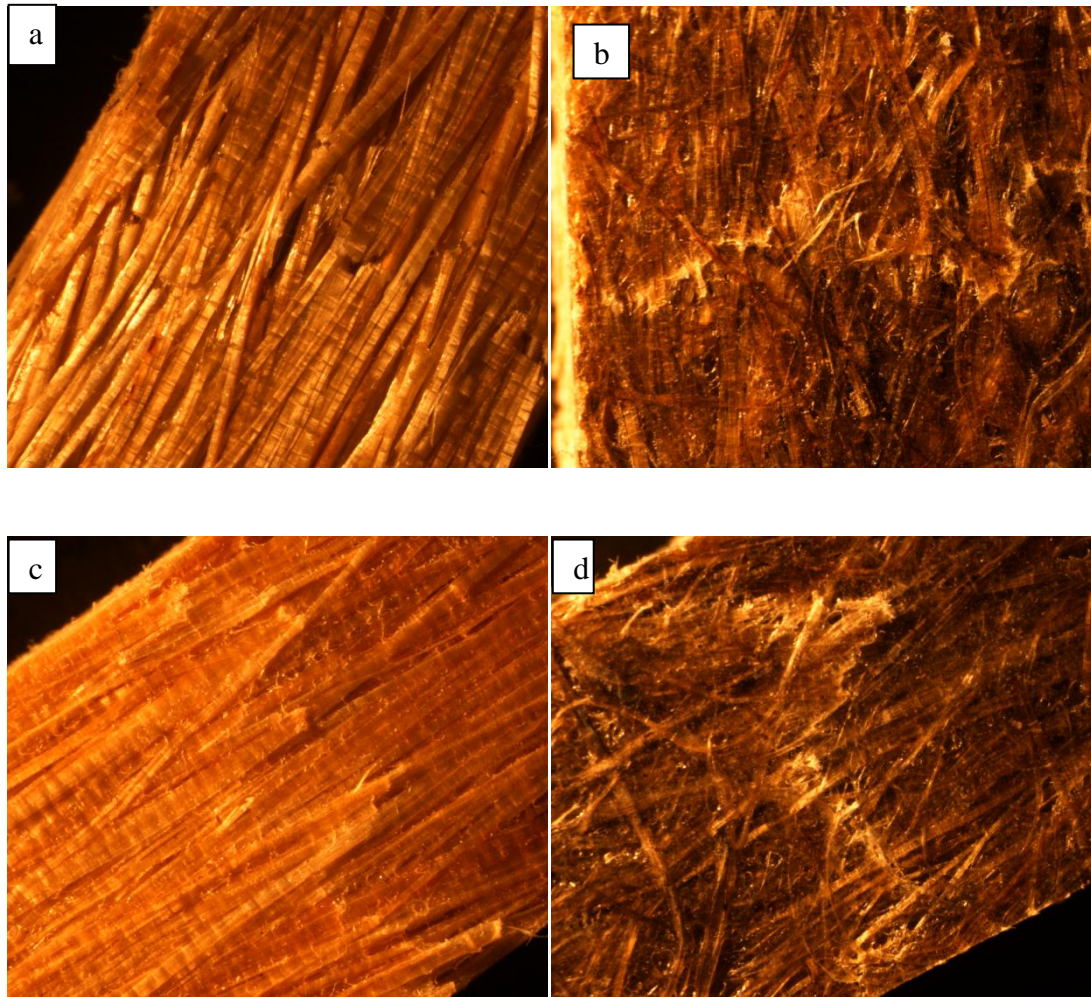


**Figure 7.8: Average stress strain curves for non-hybrid and hybrid composites**

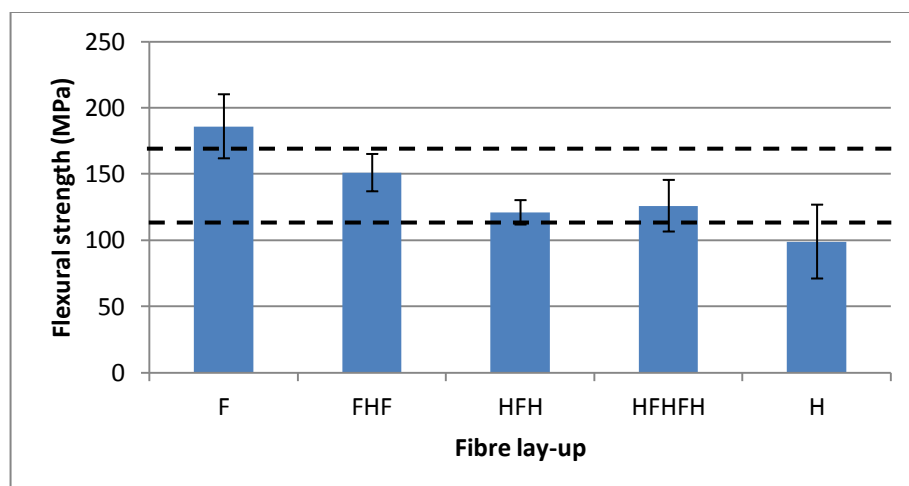
Average stress-strain curves for non-hybrid and hybrid composites are illustrated in Figure 7.8. In Chapter 5, aligned long fibre composites were found to fail when fibre failed, so composite failure strains of harakeke-only composite (LE composites) and hybrid composites were corresponding to the failure strain of harakeke fibre in composites. As can be seen in Figure 7.8, there was no increased harakeke fibre failure strain in hybrid composites with different fibre lay-up, or in other words, no FS hybrid effect was observed.

### 7.3.3 Composite flexural testing results

Non-hybrid and hybrid composite samples did not fully fracture during flexural testing but micro cracking appeared on the tension surface as shown in **Figure 7.9**



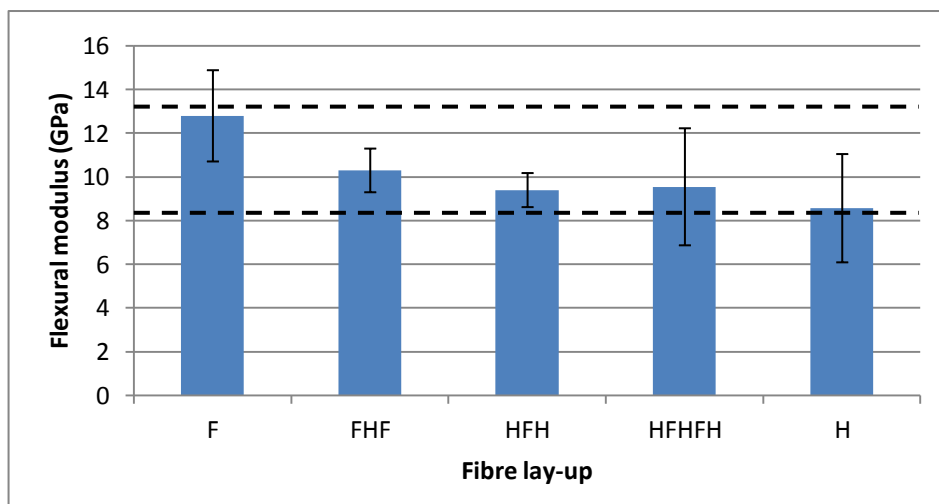
**Figure 7.9: Tension surface micrograph of composites after flexural testing: (a) harakeke-only F, (b) hybrid HFH, (c) hybrid FHF and (d) hemp-only H**



**Figure 7.10: Composite flexural strength versus fibre lay-up. Error bars each denote  $\pm 1$  standard deviation.**

Figure 7.10 presents average flexural strengths for non-hybrid and hybrid composites. It can be seen that flexural strength of harakeke-only composites was higher than that for hemp-only composites as tensile strength. Flexural strength of hybrid biocomposites with different fibre lay-up was between those for harakeke-only and hemp-only composites. The flexural strength of the hybrid FHF was the highest among hybrid composites whilst the difference between flexural strengths of HFH and HFHFH hybrid composites was not significant as confirmed by Student t-test.

As can be seen in Figure 7.11, the flexural moduli of non-hybrid and hybrid composites share the same trend with flexural strength. According to Student's t-test, there was no statistically significant difference between flexural moduli for HFH and HFHFH hybrid composites. As discussed in Chapter 6, flexural properties of sandwich hybrid composites depend on outer fibre layers due to the effect of second moment of area, therefore they did not follow the Rule of Mixtures although their value fell between the lower bound and higher bound ROM lines.

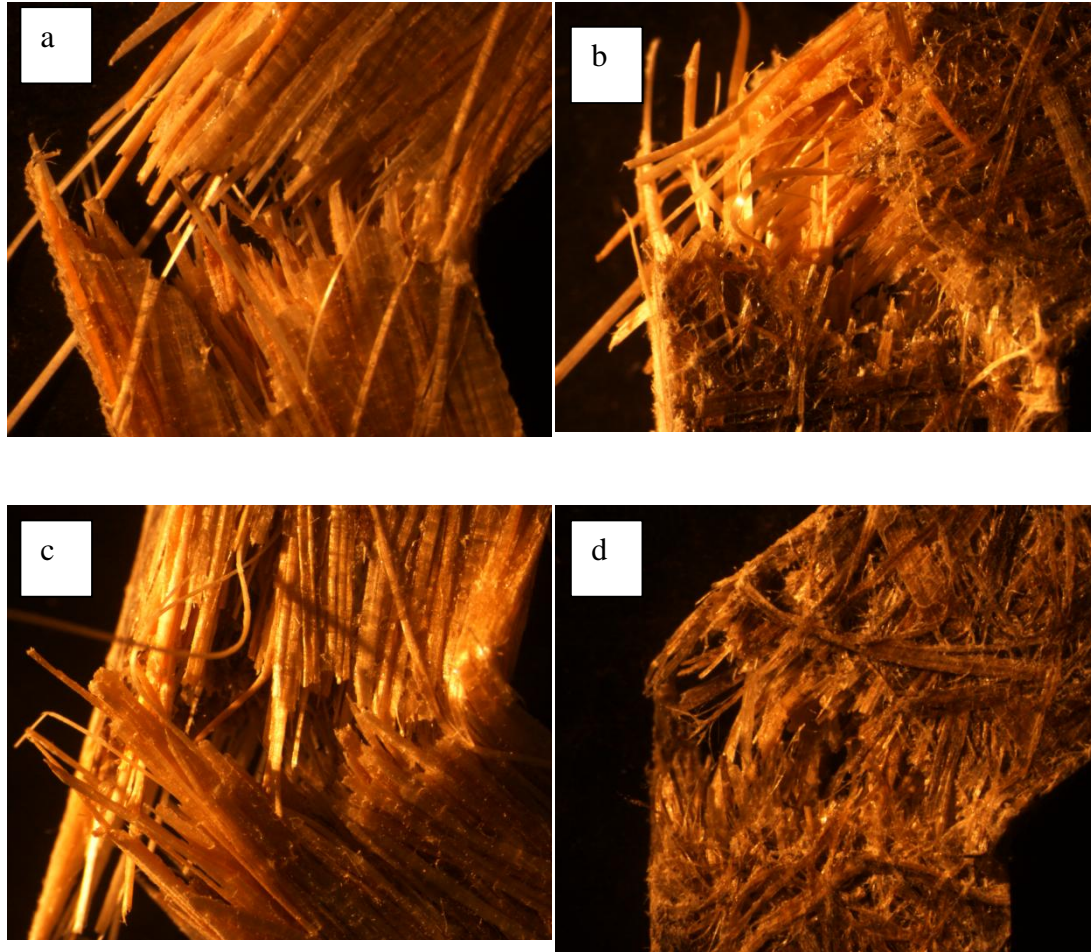


**Figure 7.11: Composite flexural modulus versus fibre lay-up. Error bars each denote  $\pm 1$  standard deviation.**



### 7.3.4 Impact strength

Micrographs of impact tested composites are presented in **Figure 7.12**.

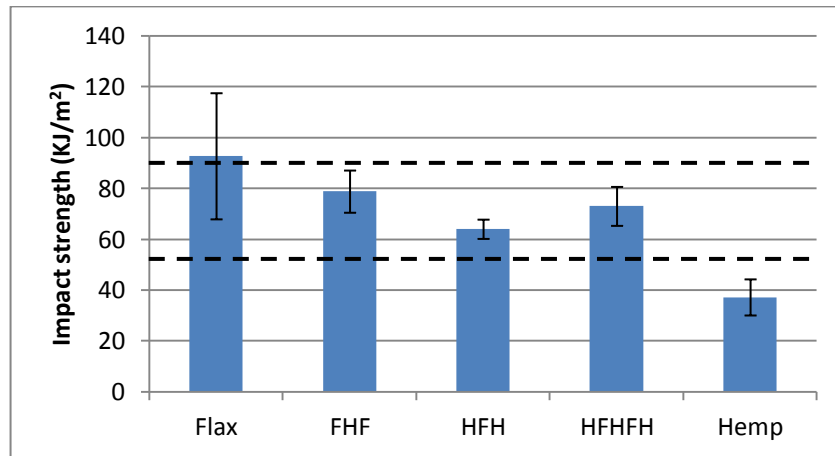


**Figure 7.12: Micrographs of composites after impact testing: (a) harakeke-only F, (b) hybrid HFH, (c) hybrid FHF and (d) hemp-only H**

As can be seen, samples were not broken into two pieces completely but some fibres linked two ends of the samples together. This mode of failure was associated with high energy absorption [141]. The micrographs also show fibre pullout due to the fracture of long fibres during impact testing. Average impact strengths of hybrid biocomposites, harakeke-only and hemp-only composites are presented in Figure 7.13. It can be seen that the impact strength of harakeke-only composites (F) ( $92.7 \text{ KJ/m}^2$ ) was higher than that of hemp-only composites (H)

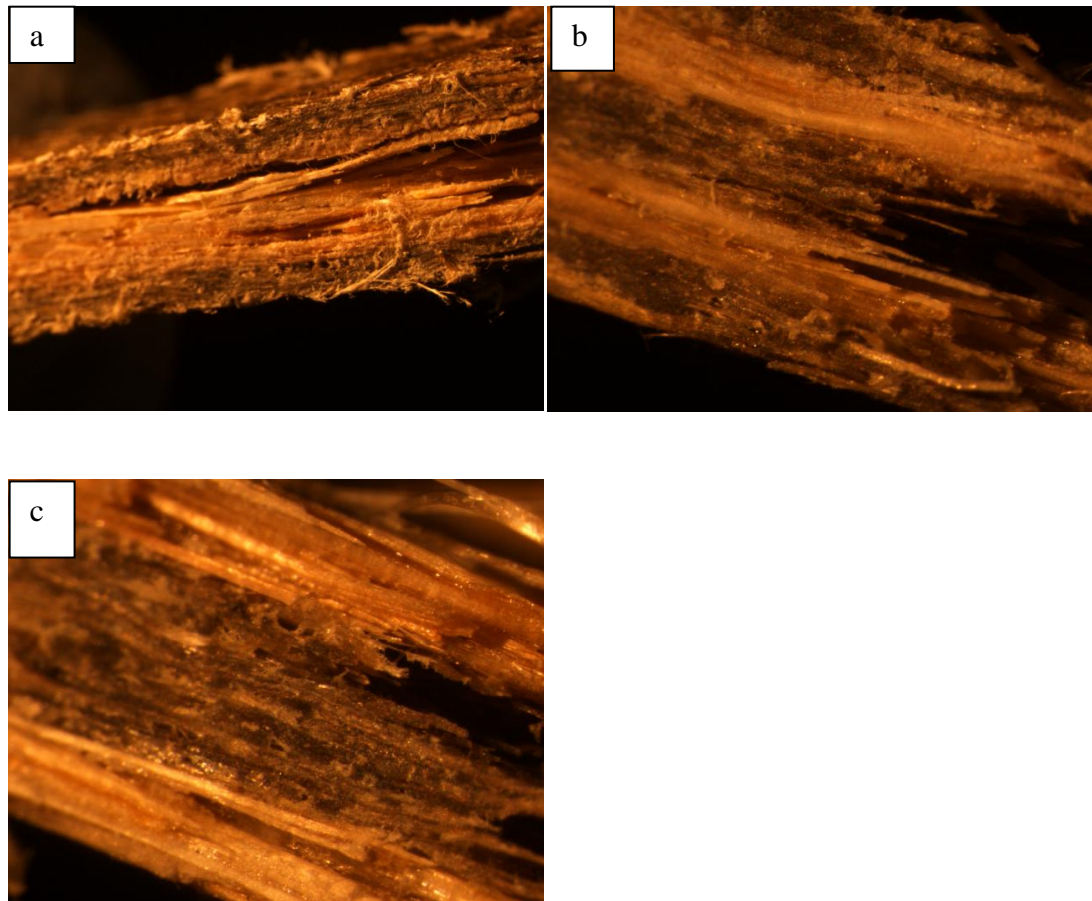


(37.2 KJ/m<sup>2</sup>). Composite modulus, fibre length and fibre tensile strength are important factors to control the fracture energy of composites [141].



**Figure 7.13: Impact strength versus fibre lay-up. Error bars each denote  $\pm 1$  standard deviation.**

Those properties of harakeke, which were found to be better than hemp as shown in Chapter 3, appear to have contributed to the higher impact energy for harakeke-only composites than for hemp-only one. The impact strength of hybrid biocomposites was greater than that for hemp-only composites but smaller than that of harakeke only composites. Among hybrid composites, impact strength for HFH hybrid bicomposite was the lowest while these for FHF and HFHFH were not significantly different according to the Student's t-test. This could be due to delamination between harakeke (bright colour) and hemp (dark colour) layers in HFH hybrid as shown in Figure 7.14. It can be seen in Figure 7.13 that impact strengths of hybrid composites with different lay-up were between lower bound and upper bound ROM lines and as such obeyed the Rule of Mixtures.

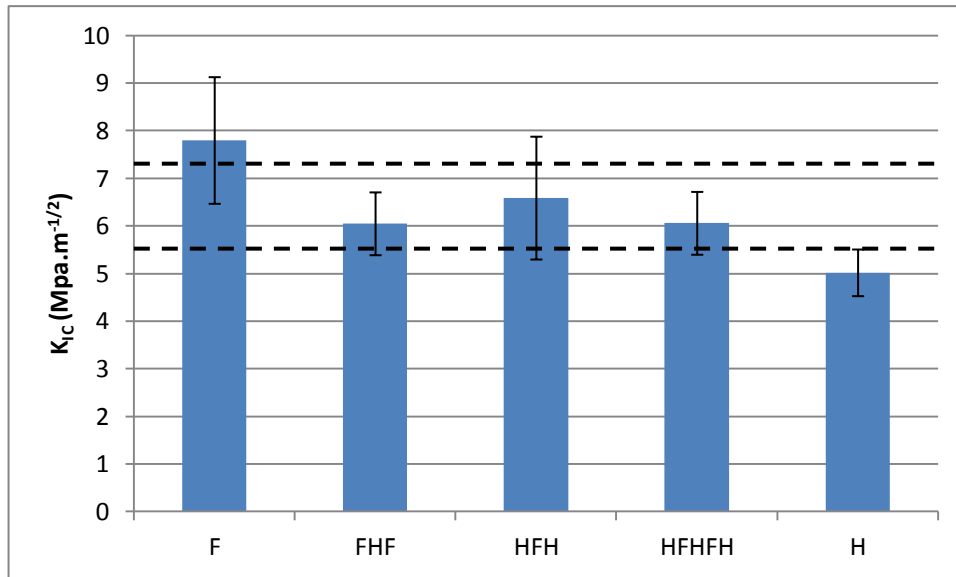


**Figure 7.14. Front edge micrographs of impact tested composites near the fracture surface: (a) hybrid HFH, (b) hybrid HFHFH and (c) hybrid FHF**

### **7.3.5 Fracture toughness ( $K_{IC}$ )**

Average fracture toughness ( $K_{IC}$ ) of non-hybrid and hybrid composites are presented in Figure 7.15.  $K_{IC}$  of harakeke-only composites was higher than of hemp-only composites. It could be due to higher strength, length of harakeke fibre compared to hemp fibre. Moreover, fibre pull-out for harakeke in composites was longer than that for hemp fibre as shown in Figure 7.16

$K_{IC}$ s for hybrid composites with different fibre lay-up were between those for harakeke-only and hemp-only composites following the Rule of Mixtures.



**Figure 7.15: Fracture toughness versus fibre lay-up. Error bars each denote  $\pm 1$  standard deviation.**



**Figure 7.16: A micrograph of FHF hybrid composites after fracture toughness testing.**

## 7.4 Chapter conclusions

The hybridisation of aligned long harakeke fibre bundles with aligned long hemp fibres in an epoxy resin was investigated. Tensile and flexural properties as well as impact strength and fracture toughness of harakeke-only composites were

found to be better than those of hemp-only composites behaved to be due to greater strength and length and better alignment of harakeke fibre compared to hemp. These properties of hybrid biocomposites followed the Rule of Mixtures. It was also found that tensile properties, flexural modulus and fracture toughness of hybrid biocomposites were not affected by fibre lay-up while flexural strength and impact strength were. Hybrid FHF with harakeke fibre at the skin possessed the highest flexural strength among the hybrids, while the flexural strengths for HFH and HFHFH with hemp fibre at the outer layers were not significantly different. The impact strength of hybrid HFH was lowest of all due to delamination between harakeke and hemp fibre layers.

## Chapter Eight: Conclusions

### 8.1 Fibre pulping

In this investigation, it was shown that thermal-alkali treatments with 2%NaOH or 5%NaOH/2Na<sub>2</sub>SO<sub>3</sub> for harakeke fibre and 5%NaOH/2%Na<sub>2</sub>SO<sub>3</sub> for hemp fibre could be used to separate fibre bundles into finer bundles and even single fibres. Fibre densities were found to increase after treatments whilst fibre diameter was retained. The NaOH treatment for harakeke fibre and NaOH/Na<sub>2</sub>SO<sub>3</sub> treatment for hemp fibre were found not to reduce the fibre tensile strength and Young's modulus whilst NaOH/Na<sub>2</sub>SO<sub>3</sub> treatment for harakeke fibre was found to reduce the fibre tensile strength considerably as well as reduce Young's modulus.

Single fibre diameters and fibre wall thicknesses were measured using a Kajaani Fibrelab electronic sequential fibre analyser which showed that fibre lumens took up a significant proportion of the cross-sectional area with 41% and 18% for single harakeke and hemp fibres, respectively. It could be considered that measurements of strength and stiffness of harakeke and hemp fibres obtained not taking this into account are underestimations to the same degree. Lumens were also found to contribute considerably to porosity in aligned long harakeke/epoxy composites.

SEM images of harakeke and hemp fibre surfaces showed that the gummy polysaccharides of lignin, pectin and hemicelluloses were removed from the fibres leaving rough surfaces containing large numbers of etched striations. Surfaces of harakeke fibres were found to be rougher than those of hemp fibres. It is thought

that the striations would provide enhanced mechanical interlocking with the polymer matrix

## **8.2 Aligned short harakeke fibre composites**

Dynamic sheet forming was used to successfully produce well aligned fibre mats which can be used as reinforcement for composites. The degree of the fibre alignment in the aligned fibre mats was assessed using the ratio between transverse tensile strength (TTS) and longitudinal tensile strength (LTS). In theory, the ratio TTS/LTS of fibre mats can vary from 0.1 to 0.9 and the lower the TTS/LTS ratio the higher the degree of fibre orientation. The ratio of 0.30 was found for the harakeke fibre mats indicating very good orientation. The alignment of harakeke fibres in aligned fibre composites was also assessed using SEM micrographs of tensile fracture surfaces of composites when tested in the longitudinal and transverse directions; more fibre ends were apparent for longitudinally tensile tested samples whilst more fibre imprints were present on transverse tensile sections confirming the orientation of fibres. The alignment of harakeke fibres in composites was further evaluated via an orientation factor ( $k_1$ ) estimated using Bowyer-Bader model. Average orientation factors of 0.53 and 0.31 were found for aligned fibre composites and random fibre composites, respectively, at a fibre content of 46wt%.

Aligned short harakeke fibres composites showed good mechanical performance; harakeke improved tensile and flexural properties of neat epoxy resin even at a fibre content as low as 10wt%. At this content, the longitudinal tensile strength and Young's modulus of composite were 1.3 and 1.2 times higher than those of neat epoxy resin, respectively, and 1.5 and 1.2 times higher than those of

transverse properties, respectively. Longitudinal tensile and flexural properties of aligned short harakeke fibre composites were found to increase as fibre content increased up to 46wt%. At this fibre content, tensile strength and Young's modulus of aligned short harakeke fibre composites were found to be 1.8 and 1.4 times, respectively, higher than those of random fibre composites, while figures for flexural strength and flexural modulus were 1.3 and 1.4, respectively. The maximum tensile strength and Young's modulus of 136 MPa and 10.5 GPa, respectively at a fibre content of 46 wt% are higher than any reported in the literature to date for natural fibre composites excluding those where hand-layup or a continuous fibre form has been produced and furthermore; these values overlap with those achieved using these procedures.

### **8.3 Aligned long harakeke fibre composites**

Aligned long harakeke fibre showed potential as reinforcement in epoxy composites. Mechanical properties of the composites were found to increase with increased fibre content. Maximum tensile strength at Young's modulus found at a fibre content of 55% was comparable to those of sisal fibre composites while their specific values can be comparable to glass fibre composites. Impact strength of 132 KJ/m<sup>2</sup> and fracture toughness ( $K_{IC}$ ) of 7.73 MPa.m<sup>-1/2</sup> at a fibre content of 63wt%, were found to be higher than any report in the literature.

The Rule of Mixtures based model was developed for predicting aligned long harakeke fibre composite strength with the assumption that composites fail when fibres with the lowest failure strains failed and considering the effect of porosity, could be used to predict tensile strength and Young's modulus of aligned harakeke fibre composites with error from 5%-24%. Porosity in the composites

was found to be influenced considerably by fibre lumens and be a function of fibre content, which affected tensile strength as well as Young's modulus of the composites.

#### **8.4 Aligned short harakeke/hemp fibre hybrid biocomposites**

Tensile properties, impact strength and fracture toughness of aligned short harakeke/hemp hybrid composites were not influenced by fibre lay-up, while flexural properties were.

Aligned short harakeke/hemp hybrid composites were shown to be able to provide a good compromise of mechanical properties between harakeke and hemp composites. It was found that harakeke increased the tensile and flexural strengths whilst hemp fibre improved the Young's modulus, flexural modulus, impact strength and fracture toughness of the hybrid composites.

The hybrid effect based on fibre failure strain was not observed due to undetermined initial fibre failure strain in hybrid composites. Based on the Rule of Mixtures, a positive hybrid effects were observed for flexural modulus and fracture toughness at different relative harakeke fibre contents and a negative hybrid effect was observed for flexural strength at a relative harakeke fibre content of 25% and a ROM positive effect at the harakeke content of 75% whilst tensile and impact properties obeyed the Rule of Mixtures.

#### **8.5 Aligned long harakeke/hemp hybrid biocomposites**

The hybridisation of aligned long harakeke fibre bundles with long aligned hemp fibres in an epoxy resin was investigated. Tensile and flexural properties, impact strength and fracture toughness for hybrid composites with different lay-ups were



found to be higher than those for hemp-only composites but lower than those for harakeke-only composites following the Rule of Mixtures, while a negative ROM hybrid effect was observed for failure strain of hybrid composites with different fibre lay-ups. It was also found that tensile strength, Young's modulus, flexural modulus and fracture toughness of hybrid biocomposites were not affected by fibre lay-up while flexural strength and impact strength were.

It is believed that all of the research objectives stated in the introduction have been met with the completion of this thesis. Harakeke fibre has shown potential as reinforcement for polymer composite materials. A greater understanding of mechanical properties of harakeke fibre reinforced epoxy composites and harakeke/hemp hybrid composites has been achieved, and it is believed that advances in the mechanical properties of such composites have been attained. Several original contributions have also been made. Firstly the effect of fibre lumen on tensile strength and Young's modulus of natural fibres and porosity in composites has been presented. Secondly, the Rule of Mixtures based model has been developed to predict tensile strength and Young's modulus of aligned long harakeke composites with the assumption that composites fail when fibres with the lowest failure strains failed. Thirdly, aligned short natural fibre mats produced using a Dynamic Sheet Former are shown to have the potential to produce high performance natural fibre composites with very high fibre orientation factor. Fourthly, aligned short natural fibre hybrid composites have been manufactured and evaluated including assessment of the hybrid effect. Finally, impact strength and  $K_{IC}$  of harakeke fibre composites have been reported for the first time.

## Chapter nine: Recommendations and Future works

The results obtained during the course of this research have laid an important platform to further improve the properties of harakeke/epoxy composites as well as to further assess hybridisation of harakeke fibres with other natural fibres. Some recommendations for future work are as follows:

- although aligned fibre mats produced using a dynamic sheet former (DSF) were found to be successful in manufacture of high performance short harakeke composites, there is still some work which can be conducted to improve performance of the composites such as optimising parameters of DSF including drum speed, velocity of fibre flow and fibre concentration to further improve fibre alignment.
- the effect of single fibre length on fibre orientation and composite properties could be further investigated.
- producing aligned natural fibre mats from other natural fibres using DSF for reinforcement in composites and assessing performance of their composites.
- methods separating harakeke fibre bundles into single fibres without using chemicals such as mechanical, thermal and enzyme methods or a combination of these could be developed to enhance the environmental friendliness of short harakeke fibre composites.
- developing methods to reduce harakeke fibre bundles to finer bundles and simultaneously remove non-fibre components such vascular bundles and

sheath cells to improve dispersion of long harakeke fibre in composites and the fibre/matrix interfacial bonding and as such improve composite properties.

- other matrices than epoxy resin could be considered to be used for harakeke fibres, especially low cost resins such as polypropylene or biodegradable resins such as PLA and tannin.
- consideration of hybridisation of two types of fibres with obviously different fibre failure strains to assess the hybrid effect such as a combination between harakeke and silk fibres or harakeke and wool fibres.
- Acoustic emission could be used to determine the time when fibres fail in composites to further investigate the failure strain based hybrid effect.

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